Adsorption capacity of the Velenje lignite: methodology and equipment

Adsorptivnost velenjskega lignita: metodologija in oprema

Janja Žula[1,*], Jože Pezdič[2], Simon Zavšek[1], Edi Burič[1]

[1]Velenje Coal Mine, Velenje, Slovenia
[2]GEORIS, Radovljica, Slovenia

*Corresponding author. E-mail: janja.zula@rlv.si

Abstract: Laboratory study of adsorption-desorption characteristics of various lignite lithotypes is very important for prevention of coal dust and gas outbursts that represent a dangerous and unpredictable phenomenon in underground mining of the Velenje lignite. The performed study consists of adsorption investigations carried out in the geotechnical laboratory of the Velenje Coal Mine (VCM). Lignite samples contained in the reaction cell were exposed for a limited time to a gas pressure of up to 100 bar. The measurements were performed on an updated instrument according to the improved volumetric gas sampling method. The gas was sampled from the reaction cell during the sorption simulation. Updating of the instrument affected positively the data quality. The performed three sets of measurements led to results that were crucial for further research. In the experiment, the amount of adsorbed and desorbed gas was calculated from the pressure difference in the known cell volume. The obtained results could permit the risk assessment of possible coal dust and gas outbursts. The performed tests shall enable a more exact determination and understanding of gas effects, possibly add some new knowledge to understanding of the dangerous phenomena, maybe also improve their prediction and lead to better safety in mining.

Izvleček: Laboratorijske raziskave adsorpcijsko-desorpcijskih lastnosti različnih litotipov lignita v Premogovniku Velenje so zelo pomembne pri raziskovanju in preprečevanju izbruhov plina in premogovega prahu, ki so nevarni in nepredvidljivi pojavi pri rudarjenju v omenjenem premogovniku.

Original scientific paper

Raziskovanje je zajemalo meritve sorpcijskih lastnosti lignita v geotehničnem laboratoriju Premogovnika Velenje, kjer so bili različni vzorci lignita zaprti v reakcijski celici in obremenjeni z do 100 bar plina za določen čas. Vzpostavili smo sistem meritev na posodobljeni napravi, izpopolnili volumetrično metodo in način vzorčevanja plina iz reakcijske celice med potekom simulacije sorpcije. Posodobitev naprave je vplivala na kvaliteto pridobljenih podatkov. Izvedli smo tri sklope meritev, ki so pokazali odločilne rezultate za nadaljnje raziskave. Po končanih meritvah sorpcije smo matematično določili količino adsorbiranega in desorbiranega plina iz razlike tlaka plina v znanem volumnu celice. S količino plina ocenimo stopnjo tveganja pri odkopavanju različnih plasti premoga, kjer lahko pride do vdora plina. S temi poskusi bo mogoče bolj natančno opredeliti in razumeti plinske efekte v Premogovniku Velenje in morda tudi prispevati k razumevanju nevarnih dogodkov, njihovemu morebitnemu napovedovanju in s tem k večji varnosti.

Key words: sorption, lignite, lithotype, laboratory experiments, Velenje Coal Mine – Slovenia

Ključne besede: sorpcija, lignit, litotip, laboratorijski poskusi, Premogovnik Velenje – Slovenija

Introduction

Various lignite lithotypes are of microporous structure in which the gas occurs compressed in the pores, cleats and capillaries. The gas in these tiny spaces can be in gaseous, liquid or even solid state. The basic lignite lithotypes are determined macroscopically, and they can be recognized with an unaided eye. The lithotypes are named according to the classification of the International Committee for Coal and Organic Petrology (ICCP, 1993) (e.g. in Taylor et al. (1998), p. 280).

A gas-mix accumulated in a coal, termed as the coalbed gas, can be of various origins and migration paths and this is also an outstanding fact in the case of the Velenje lignite. This thematic was thoroughly studied by Pezdič and his co-workers for almost 15 years - from 1998 onwards - and is in details well documented in yearly-made elaborations for the VCM company as "Monitoring of gas components" in the Velenje Coal Mine as well as published in papers by Kanduč et al. (2003), Kanduč (2004), and Kanduč & Pezdič (2005). The content presented in this paper is mainly a summary from the B.Sc. thesis work of the first author (Žula, 2006), which was also mentored by professor Pezdič.

Coalbed gases, together with rock-mechanical properties of the lignite in different areas of the Velenje lignite mining are highly responsible for dynamical processes during advancement of mine workings. Among them, the most dangerous events are sudden coal-falls, gas exhalations, gas and lignite outbursts, and pillar chocks. This thematic was studied and evidenced for decades. More recently, it was summarized and interpreted in representative works of LIKAR (1995), ZAVŠEK (2004) and in many working reports and studies cited by these two authors. In connection with rock-mechanics, LIKAR and his co-workers studied in the 1990 and 2000 also sorption of gases in lignite at different strain conditions (PEZDIČ et al. 1999 a, b). Results and long-term investigation are also archived at the VCM in the form of annual reports and elaborations.

The coalbed gas occurs in pores and cleats of coal under the lithostatic pressure of rocks above the coal seam and under the pore pressure. When pressure decreases, the gas is released from the coal, and can migrate freely. Migration of gas is especially enhanced in tectonized zones along fault systems. Gases can be accumulated in the void volumes (pores, cleats, crushed zones, chambers) of various sizes both adsorbed on the surfaces and dissolved in water. Studying gases in coals and their adsorption/desorption behavior is of great interest in the last two decades especially in connection with efforts to assess potential of coals as a geological medium for eventual storage of CO_2, particularly in combination with enhanced methane recovery. In this context, at least studies of sorption on different coals worldwide should be mentioned here: LITWINISZYN (1990), GAMSON et al. (1996), PEZDIČ et al. (1999b), MASTALERZ et al. (2004), MAJEWSKA et al. (2009), GRUSZKIEWICZ et al. (2009), WENIGER et al. (2010). In 2009, a special issue of the International Journal of Coal Geology (Vol. 77/1–2) was devoted to CO_2 sequestration in coals and enhanced coalbed methane recovery.

The origin of gases can be inferred from the isotope composition of its gas components. Such a pioneering study for the Velenje lignite was carried out by KANDUČ & PEZDIČ (2005). On the basis of carbon isotope composition of carbon dioxide and methane they concluded that the following types of origin of CO_2 and methane can be recognized: microbial methane and CO_2, methane generated by microbial CO_2 reduction and/or methane affected by processes of oxidation, and endogenic CO_2.

The isotope composition of coal-bed gases is affected by a range of factors: the original organic matter composition, temperature, Eh-pH conditions, microbiological activity, so called secondary processes (diffusion, migration,

oxidation), and by mixing of gases of various origin (Kanduč & Pezdič (2005); and references there-in).

Gases in the Velenje basin are of a highly variable composition both within the lignite seam and the non-coaly basin sediments. According to data from Kanduč & Pezdič (2005), the CDMI (carbon dioxide to methane index expressed as $\varphi(CO_2) \times 100 / \varphi(CO_2 + CH_4)$ varies between 80 % and 99 % in the lignite-seam gases (with very rare exceptions of the CDMI being considerably below 80 %), whereas this index is from 1 % to ca. 55 % in the gases as coming from the subsurface wells penetrating different basin sediments and the pre-Pliocene basement rocks. Considerably variable is also content of N_2, i.e. between 0 % and almost 55 % (as reported in Kanduč & Pezdič (2005)), but this range is highly dependent on the sampling approach (see samples of the A and B types in Table 1 in Kanduč & Pezdič (2005)). It is evident that the gases in the Velenje lignite (as well as in other lithologies) have various origins and are affected by possible mixing and changes owing to different physicochemical properties of methane and CO_2 during gas migration (Kanduč et al. (2003), Kanduč & Pezdič (2005)). Amount of the gas sorbed in the coal depends also on pressure, temperature, mineral matter, moisture and the coal lithotype. Rate of achieving the adsorption equilibrium depends on the

sorption rate in pores and on gas diffusion into the porous coal matrix (Pezdič (1999), Kanduč (2004)).

In closed systems, as e.g. in areas of still un-excavated and relatively undisturbed parts of coal/lignite seams, accumulations of gases at high pressures may occur. In a final stage, they may attain or exceed the value of the lithostatic pressure. Such circumstances are characteristic for zones ahead of mining longwalls and mine-road faces (Kanduč et al. (2003), Kanduč & Pezdič (2005)). Opening of such a zone is often a highly dynamic process that can lead to a coal-dust and gas outburst. As the total and partial pressure of the adsorbed gases decreases, this can affect a wider area of the coal seam. In dependence of conditions and properties of the coal matter, the gas desorption can be a sudden, momentary event (e.g. Likar (1995), Zavšek (2004)).

Sorption method, equipment and measurements

The quantity of adsorbed gas was determined according to the sorption method, as described in Pezdič et al. (1999b). For measuring the adsorption-desorption properties of various lignite lithotypes at high pressures (up to almost 100 bar), the volumetric method was applied.

For calculating the quantities of adsorbed gas the theoretical bases were used as cited in Pezdič et al. (1999b) and in Žula (2006), taken mostly after Moore (1974). We proceeded from the general gas law (1) and the real gas law (2) (see e.g. in Lazarini & Brenčič, 1992):

$$PV = nRT \qquad (1)$$

For gases deviating from ideal conditions the gas equation for real gases is used, the so-called van der Waals equation.

$$(P + an^2/V^2)\,(V - nb) = nRT \qquad (2)$$

We calculate the volume of the adsorbed gas V_a after equation (3):

$$(P_0 - P_t)\,V_{free} = V_a\,P_a \qquad (3)$$

P_0 is the initial pressure, P_t is the pressure determined after a certain time period t, P_a is 1.013 bar and V_{free} the volume in autoclave.

Amount of the adsorbed gas is given in three different ways (4, 5, 6):

$$V_{adsorb} = V_a/m_{material} \quad (L/\,kg) \qquad (4)$$
$$n = V_{adsorb}/V_0 \qquad (mmol/kg) \qquad (5)$$
$$m_{gas} = nM/1000 \quad (g/kg) \qquad (6)$$

Equipment
The apparatus for gas sorption measurements has been set in the Geotech-nical laboratory of the VCM. Measurements of sorption were performed on the third modification of the high-pressure system as initially used by Pezdič in 1998 (Figure 1).

The apparatus has been meanwhile improved by adding a new measurement registering system. Readings of pressure and temperature are now directly transformed to graphic signals that are continuously monitored on a display (Figure 2). In this way, by updating the computer program (Supovec & Filipič, 2004), detection of temperature and pressure signals became more accurate, since being performed in one second time intervals. This permitted registration of the most important data during the first minute after dosing, when adsorption is at the highest. Added were also two additional temperature sensors for registration of temperature in the system and in the room. The system temperature (T_{system}) is measured on the housing of autoclave with a temperature sensor (PT1000) fixed to the housing. An additional construction improvement was done on net volume of autoclave. The robe for pressure measurements was placed closer to autoclave, and the volume reduced by valve (V). The additional valve on the autoclave permits the extraction of gas during adsorption (Figure 3).

Figure 1. Modernized apparatus for sorption measurements - autoclave, probe, valves, software application
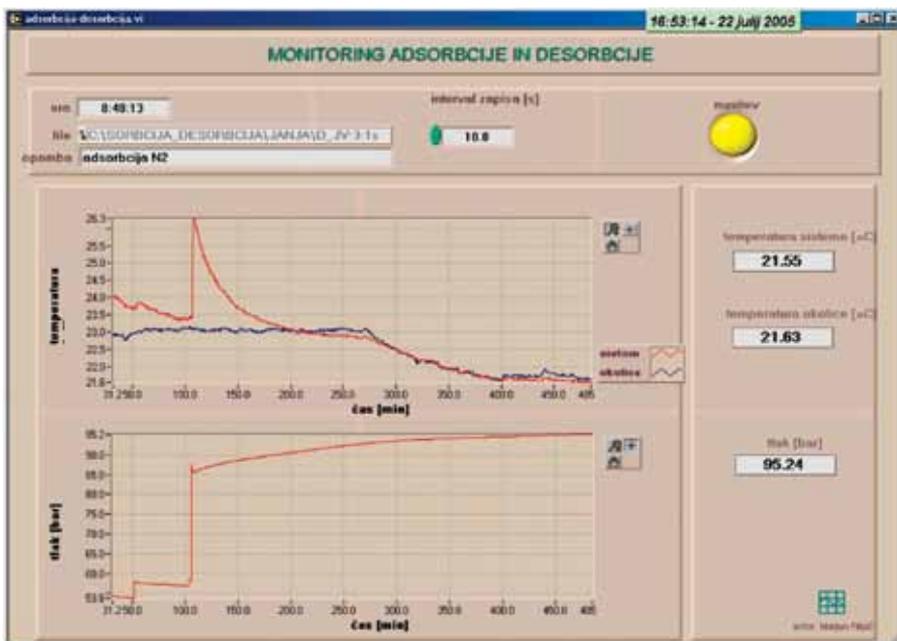
Figure 2. Computer output of pressure and temperature measurements (SUPOVEC & FILIPIČ, 2004).

Manometer

System with a valve (V)

Probe

Valve for gas

Reaction cell -autoclave
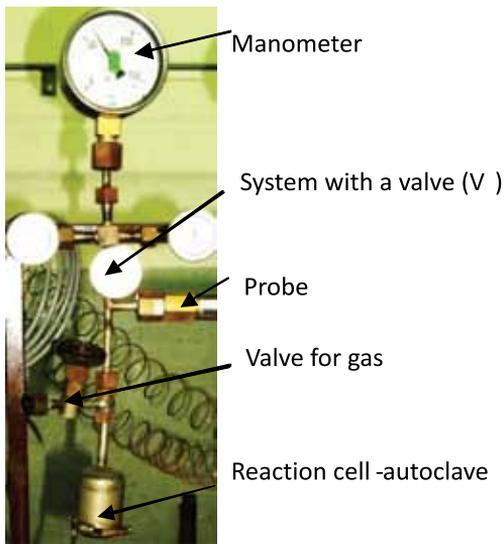
Figure 3. System with the reaction cell

Sampling of lignite
Lignite was sampled in borehole cores, and from mine road and longwall faces (Table 1).

Six distinct samples differing in their lithotype composition were prepared and classified according to the ICCP classification (1993) (in: Taylor et al. (1998), p. 280). Sample 1 was pure xylite (X), and samples 3 and 4 were xylite-rich and xylite very rich lignite lithotypes. Samples 2, 5 and 6 were lithotypes of fine detrital lignite. Among them, sample 2, which was taken from a fault zone, and sample 5, both exhibited a pronounced degree of gelification. Generally speaking, fine detrital and gelified lignite is more characteristic for the upper and the inner part of the Velenje lignite seam,

whereas more or less xylite-rich lignite predominates in the lower and the outer part of the seam (Markič & Sachsen-hofer, 1997, 2010). In Table 1, petrographic composition is also expressed in terms of lithotype components (in percents and by code values) as introduced by Markič et al. (2001) and Markič & Sachsenhofer (2010).

For a sorption measurement around 100 g of crushed lignite material of 2−4 mm grain size was used.

Measurement process
The whole sorption measurement process consisted of five steps. In the first step, after dosing to ca. 60 bar CO_2, adsorption was measured for 45 min. In the following step, dosing to ca. 60 bar CO_2 was repeated and adsorption was measured again for 45 min. After that, the type A gas sampling was performed. As during the gas sampling some pressure in the flask was lost, the missing CO_2 was replaced.

Into the equilibrated sample, we added nitrogen N_2 overpressure up to a total pressure around 85 bar. Adsorption of the gas mixture ($CO_2 + N_2$) lasted for additional six hours. After completed adsorption of the ($CO_2 + N_2$) gas mixture, we performed the B type gas sampling and then exposed the sample to atmospheric pressure (1 bar). Desorption followed, and was measured for 15 h.

Table 1. Samples chosen for sorption tests

Sample 1: Xylite; X 100 %

Petrographic code: 3

Sample 2: Fine detrital gelified lignite **(from a fault zone !)**

fD 90 % G 10 %

Petrographic code: 9.5

Visible are milimeter thick white CaCO3coatings over vegetal remains

Samp. 3: Xylite-rich lignite

dXxD 20 % fD 80 %

Petrographic code: 8.4

Samp. 4: Xylite very rich lignite

X 80 % dXxD 10 % fD 10 %

Petrographic code: 3.75

Samp. 5: Fine detrital gelified lignite

X 15% fD 65% G 20%

Petrographic code: 9.5

Visible are milimeter thick white CaCO3coatings over vegetal remains

Sample 6: Fine detrital lignite

dXxD 7% fD 93 %

Petrographic code: 8.95

Sampling of gas components from an autoclave

For gas sampling during sorption a special equipment shown in Figures 4, 5 was used. Gas capture from an autoclave was a two-step procedure. First, the gas was captured into a piston ampoule (1 bar), and then transferred to a laboratory ampoule. Two types of sampling were differentiated, the type A and type B sampling.

The type A sampling was carried out at the end of the second CO_2 adsorption phase i.e. after 90 min from the beginning of the adsorption measurements.

The type B sampling was capture of gas mixture ($CO_2 + N_2$) in autoclave. It was carried out 6 h after N_2 dosing, just before desorption.

Gas analysis was performed on a homemade NIER mass spectrometer at the J. Stefan Institute in Ljubljana.

RESULTS

Because gas sorption in a coal is dependent on coal´s solid matter composition, moisture content, pressure, time and kind of gas dosed, and because gas composition is alternating due to dosing of different gases and due to adsorption/desorption effects, three sets of measurements were performed. The 1st set represents measurements at varying moistures, the 2nd set comprises measurements on various lignite lithotypes, and the 3rd set represents comparison of composition of gases as sampled at varying pressures (ŽULA, 2006).

First set of measurements

The 1st set of measurements was done on sample N° 3 (see Table 1) of the following lithotype composition: fD 80 % dXxD 20 %. In order to study influence of moisture on sorption, the whole sample was split into three

Figures 4. (left) and **5.** (right): Gas sampling into a piston ampoule (1 bar) from autoclave (at 60 bar to 100 bar), and then transferring of gas to a laboratory ampoule.

parts to measure moisture contents at three stages/conditions:

- at the initial stage (sample-part S-1),
- after moistening with 20 mL of distilled water, before sorption (sample-part M-1),
- after moistening with 10 mL distilled water, after sorption (sample part M-2).

Measurements were performed by a simple experiment. As gas, only CO_2 was used. The autoclave with lignite sample was dosed by CO_2 and left for 45 min for the adsorption to take place. The same time duration was applied for desorption.

The results are given in Tables 2−4:

Moisture content at the as received (a. r.) basis of the "initial" sample-part S-1 was 50.00 % (Table 2). This moisture content is very close to a real bed-moisture content (at the ash-free basis) as typical for the Velenje lignite regarding its coalification rank (Markič & Sachsenhofer (2010), p. 141-153).

Additional moistening of the sample-part M-1 with 20 mL distilled water (Table 3) resulted in an increase of moisture from 50.00 % (S-1) to 83.60 % (M-1). Additional moistening of the sample-part M-2 with "only" 10 mL distilled water

Table 2. Measurement results for S-1

Sample	Test	m(p1) (g)	m(p2) (g)	P_0 (bar)	$\Delta p_{ads.}$ (bar)	*Ads.* (g/kg)	$\Delta p_{des.}$ (bar)	*Des.* (g/kg)	Moisture1 (%)	Moisture2 (%)
S-1 a. r. moisture	CO_2	57.52	57.62	52.69	−1.30	**2.47**	1.39	**1.65**	**50.00**	**42.25**

Table 3. Measurement results for M-1

Sample	Test	m(p1) (g)	m(p2) (g)	P_0 (bar)	$\Delta p_{ads.}$ (bar)	*Ads.* (g/kg)	$\Delta p_{des.}$ (bar)	*Des.* (g/kg)	Moisture1 (%)	Moisture 2 (%)
M-1 a.r. moisture + 20 mL distilled water	CO_2	58.71	58.80	55.05	−4.05	**7.48**	2.71	**5.16**	**83.60**	**81.02**

Table 4. Measurement results for M-2

Sample	Test	m(p1) (g)	m(p2) (g)	P_0 (bar)	$\Delta p_{ads.}$ (bar)	*Ads.* (g/kg)	$\Delta p_{des.}$ (bar)	*Des.* (g/kg)	Moisture1 (%)	Moisture 2 (%)
M-2 a.r. moisture + 10 mL distilled water	CO_2	59.98	60.12	52.98	−2.78	**5.10**	2.51	**4.61**	**59.74**	**59.49**

(Table 4) resulted in an increase of moisture from 50.00 % (S-1) to "only" 59.74 % (M-2). Both additionally moistened sample-parts showed significantly larger adsorption and desorption than the initial sample (S-1) (Tables 2−4). CO_2 adsorption in additionally moistened sample-parts M-1 and M-2 was 2 to 3 times greater (more effective) than in S-1, and similarly was desorption. After sorption, moisture content of the sample-parts was measured again ("moisture 2" data in Tables 2−4). After sorption, the moistures decreased as follows: in sample S-1 for 7.75 %, in sample (M-1) for 2.58 %, and in sample M-2 for 0.25 %.

Second set of measurements
Sorption measurements were performed on six samples (1, 2, 3, 4, 5, 6), differing in lithotype composition (Table 1). Detailed measurements for all samples are given in Žula (2006), whereas in this paper, measurements for all samples are given only graphically (Graphs 3, 4, 5), and only exampling tabular data will be presented and discussed (Table 5).

On each sample, two identical measurements were done. Between the two measurements on the same sample, slight deviations appeared - most probably due to heterogeneity of samples, different initial sample weights, dosage velocities, amounts of dosed gas, slight temperature differences and slight differences in moisture.

As an example, results for sample N° 2 are presented in Table 5.

Explanation of results in Table 5 and pressure conditions shown in Figures 6, 7, 8.

- After first dose (56.50 bar CO_2), lignite adsorbs in 45 min 3.65 bar or 6.65 g/kg (grams of gas per kilogram of coal).
- After second dose (58.15 bar CO_2), in the next 45 min, lignite adsorbs 1.28 bar or 2.33 g/kg.
- In total it adsorbs 4.93 bar or 8.98 g/kg.
- Third dose (58.60 bar CO_2) represents a maximal filling of reaction cell with CO_2.
- The fourth stage is dosing 87.26 bar N_2 onto equilibrated sample. At the first moment, in less than 1 minute, the total pressure decreases for 2.15 bar, but then, after ca. six hours, it increases up to 95.12 bar. In total, 10.02 bar of gas or 18.25 g/kg (grams of gas per kg of coal) became released. A momentary pressure decrease after N_2 dosing is also characteristic for other samples (as measured by Žula (2006)). Subsequent slowly permanent increase in pressure for about 10 bar to 11 bar in six hours or so, indicates release of gas from coal. This is maybe the most important phenomenon in sorption investigations of the Velenje lignite. It was already clearly

Table 5. Adsorption and desorption key data for sample Nᵒ 2 from Table 1 based on two repeated measurements (2-1 and 2-2). Sample composition: fD 90 %, G 10 %, autoclave volume: 105 mL, coal mass: 60 g, environmental temperature: 22 °C, V_0: 24.12 mL/mmol, specific mass: 1.33 g/cm³, free volume: 59.9 mL. Dots indicate gas sampling. Abbreviations W1 and W2 mean two measurements of mass of coal samples analyzed. T_{sist}/K is temperature of system in autoclave in Kelvin scale. P_1 to P_4 are starting pressure (e.g. 56.50 bar) and pressure after a certain time (e.g. 52.85 bar). P_x is increased pressure at adsorption. Δp_{ads} is difference in pressures due to adsorption, and Δp_{des} is difference in pressures due to desorption. Ads. and Des. are amounts of adsorbed and desorbed gas(es), respectively, expressed in grams of gas per kilogram of lignite.

Sample	Test	W1 (g)	W2 (g)	Time (h)	Tsist. (K)	P (bar)	Δp ads. (bar)	Ads. (g/kg)	Δp des. (bar)	Des. (g/kg)
2-1		60.0	60.11	0						
	(CO₂)			0.001	297.18	(P1) 56.50	-3.65	**6.65**		
				0.75		52.85				
	(CO₂)			0.76	296.43	(P2) 58.15	-1.28	**2.33**		
●				1.50		56.87				
	(CO₂)			1.63	295.90	(P3) 58.60				
	(N₂)			1.75	296.02	(P4) 87.26	-2.15			
				1.76		85.11				
				1.76			+10.02	**18.25**		
●				8		(Px) 95.13				
	Drop of pressure to 1 bar and desorption of gas (mainly CO₂+N₂) lasting for 15 hours								6.67	**12.09**
2-2		60.0	60.22	0						
	(CO₂)			0.001	296.72	(P1) 57.48	-2.92	**5.31**		
				0.75		54.56				
	(CO₂)			0.76	296.89	(P2) 59.05	-1.01	**1.84**		
●				1.51		58.04				
	(CO₂)			1.63	296.48	(P3) 59.55				
	(N₂)			1.76	296.56	(P4) 87.05				
						85.01	-2.04			
							+10.70	**19.48**		
●				8		(Px) 95.71				
	Drop of pressure to 1 bar and desorption of gas (mainly CO₂+N₂) lasting for 15 hours								6.89	**12.55**

Figure 6. Graphic presentation of the used starting pressures (P_1, P_2, P_3, P_4) with adsorption in particulate phase and especial event (P_x) with decrease and then increase of pressure during the adsorption process of $CO_2 + N_2$ mixture.
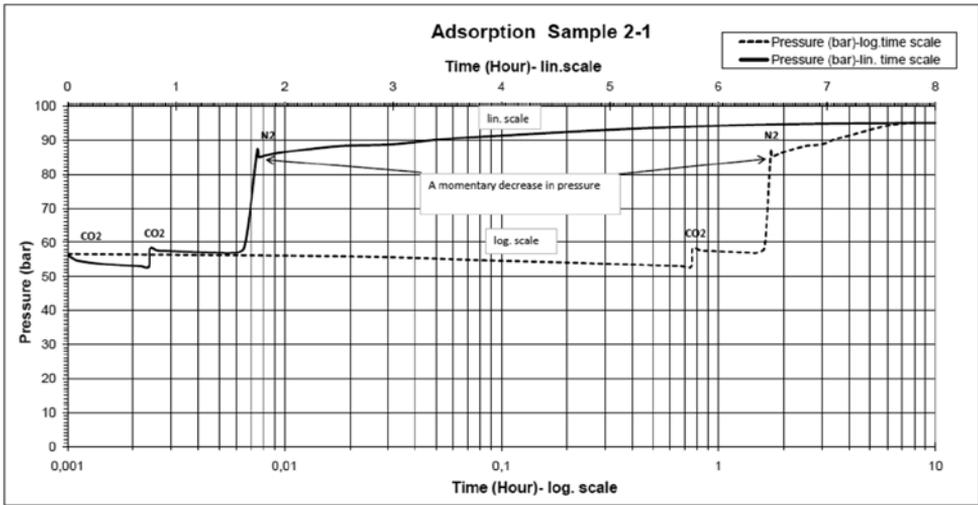
Figure 7. Pressure behaviour as measured in autoclave after 1st and 2nd dosing by CO_2, and after dosing by N_2 (in a linear and the logarithmic scale). Note that dosing by CO_2 causes adsorption of gas into coal substance (detected as two slight decreases of pressure in the first two 45 min lasting steps), and that N_2 dosing causes - after an instant time of adsorption - a release of gas from coal (detected as slight increase and then stabilizing of pressure in the time interval between 1.75 h and 8 h). Note also considerably higher pressure of N_2 dosing in comparison to CO_2.
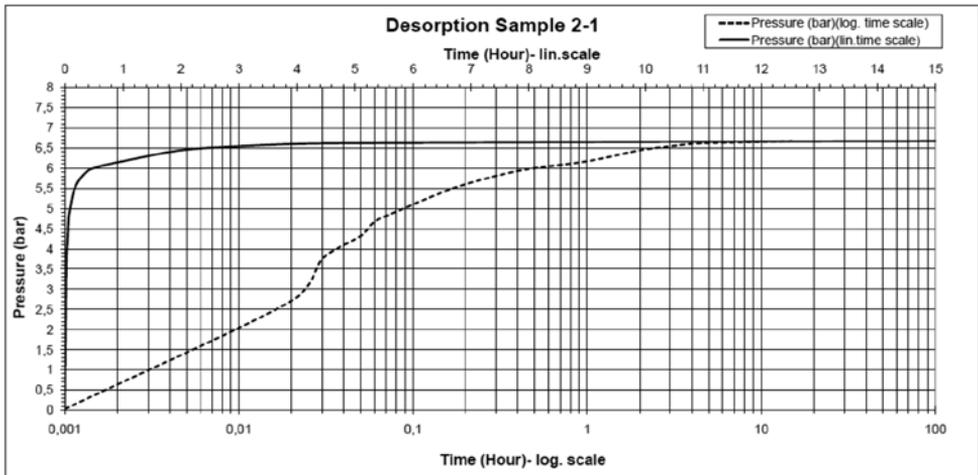
Figure 8. Desorption of gas from sample 2-1. Measurements expressed by Δ pressure values are shown in a normal linear scale and the logarithmic scale, respectively.

detected by Pezdič at el. (1999b) and was explained by different possible processes, which would need additional investigations. One explanation is enhanced release of gases from coal, and some other explanations are thoroughly given in Pezdič et al. (1999b), Pezdič et al. (2007) .

- Comparing results for sample 2-1 and 2-2, adsorption due to CO_2 dosing is slightly more effective for the first sample, whereas gas release due to N_2 dosing is somewhat higher in the second sample.
- Desorption is 6.67 bar or 12.09 g/kg in the first measurement case (2-1), and 6.89 bar or 12.55 g/kg in the second case (2-2), respectively.

Sample 1-1 and Sample 4-1:
Samples 1-1 (X 100 %) and 4-1 (X 80 %, dXxD 10 %, fD 10 %) are very similar in lithotype composition, but demonstrate quite diverse sorption characteristics (Figure 10). In the first and the second CO_2 loading stage together, sample 4-1 adsorbed 3.26 g/kg or 43.10 % less of CO_2 than sample 1-1 with 5.73 g/kg.

Additional N_2 pressure caused initially a slight decrease of the total pressure in both samples, but then the pressure started to rise (as principally visible from Figure 7), and reached after six hours the value of 90.25 bar for sample 1-1 and the value of 92.57 bar for sam-

ple 4-1. Sample 1-1 released 5.87 bar of gas or 10.44 g/kg, whereas sample 4-1 released 11.09 bar of gas or 19.01 g/kg i.e. for almost 80 % more than sample 1-1.

Proportion of released gas depends on the proportion of adsorption in the first two steps, on CO_2 compression at the time of addition of N_2 overpressure, and on velocity of gas mixture release, as we decreased the pressure to 1 bar. For the same reason desorption varies too. The desorption for sample 1-1 equals to 5.30 g/kg or to 32.78 % of the wholly adsorbed gas (5.73 + 10.44 g/kg), and for 4-1 to 3.74 g/kg or 16.80 %. Already our findings so far categorized the samples of such entirely xylite, and xylite-very-rich lignite lithotypes as the most resistant for sorption. In this sense, our present measurements published in this paper confirm this finding once again.

Sample 3-1 and Sample 6-1:
Samples 3-1 (dXxD 20 %, fD 80 %) and sample 6-1 (dXxD 7 %, fD 93 %) differ significantly in content of xylite-detrite (dXxD) component. Even though this difference (20–7 %) is numerically not very big it seems to be decisive to give the two samples quite distinctive gas adsorption characteristics.

As visible from Figure 10, total CO_2 adsorption in the sample 3-1 amounts

to 6.06 g/kg, and in sample 6-1 to 7.62 g/kg. In the second stage, less than a half of gas than in the first stage was adsorbed.

Additional N_2 pressure caused initially a slight decrease of the total pressure for both samples, but afterwards the pressure started to rise and reached the value of 95.25 bar for sample 3-1, and 93.93 bar for sample 6-1. Sample 3-1 released 16.06 g/kg of gas and sample 6-1 16.69 g/kg of gas. Desorption of the sample 3-1 equals 8.09 g/kg or 36.57 %, and of the sample 6-1 7.09 g/kg or 29.90 %.

Sample 2-1 and Sample 5-1:
Samples 2-1 (fD90%, G10%) and sample 5-1 (X 15 %, fD 65 %, G 20 %) have the same lithotype code (9.5), although their composition is different. The sample 2-1 comes from a fault zone and the sample 5-1 from a borehole. What is common to both samples is remarkable degree of gelification which was most probably enhanced due to alkalinity evidenced by e.g. carbonate coatings of vegetal remnants (see Table 1). Their gas adsorption and desorption values are much higher than for all previous samples, and this feature is connected to our opinion to gelification. Total adsorption of sample 2-1 is 8.98 g/kg, and of sample 5-1 9.80 g/kg (Figure 10). Compared to the sample 4-1 with the lowest adsorption, this is around 60 % more.
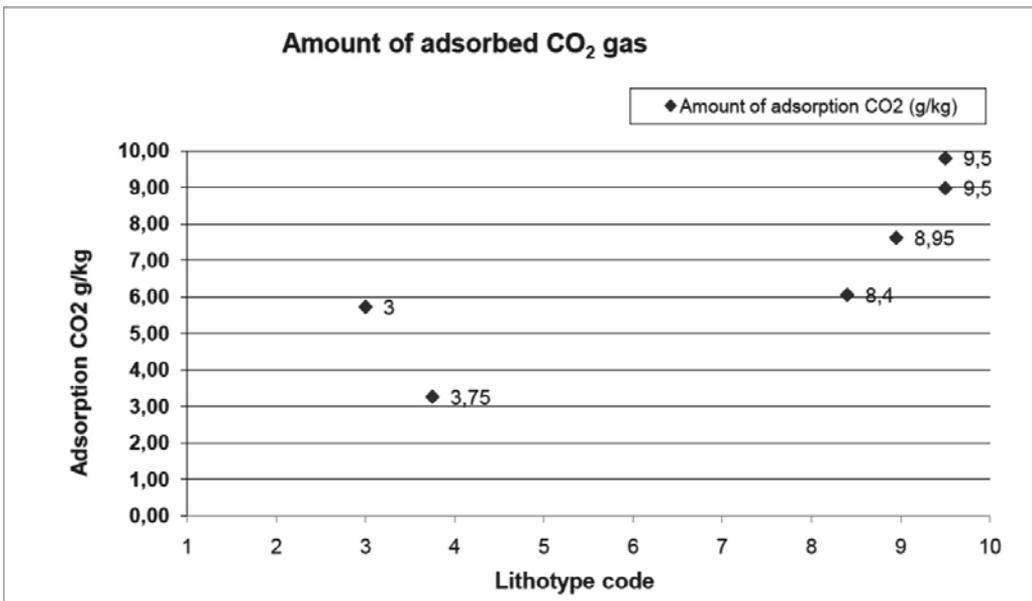
Figure 9. Amount of adsorbed CO_2 gas depends on lithotype code
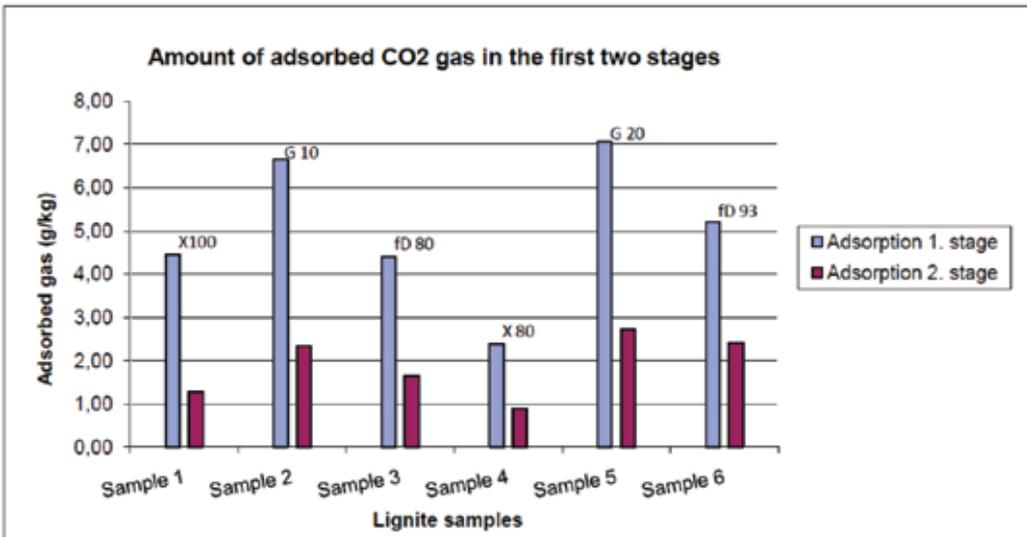
Figure 10. Amounts of adsorbed CO$_2$ as achieved by 1st and 2nd step of dosing by CO$_2$ at pressures of between 55 bar and 59 bar. Time of adsorption was 45 min for each step.
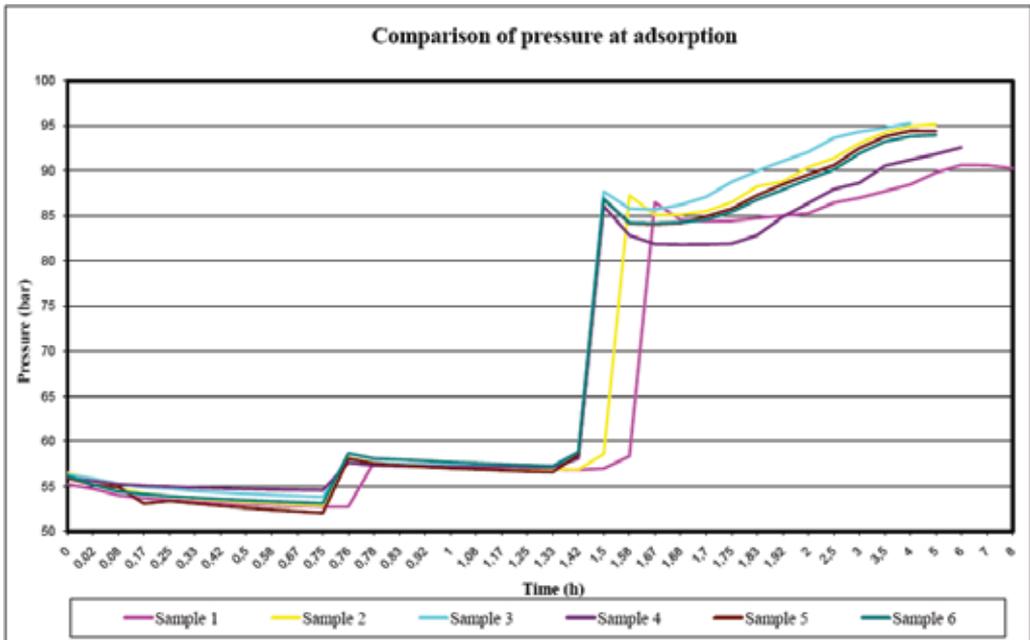
Figure 11. Pressure-to-time behaviour for all samples during adsorption.
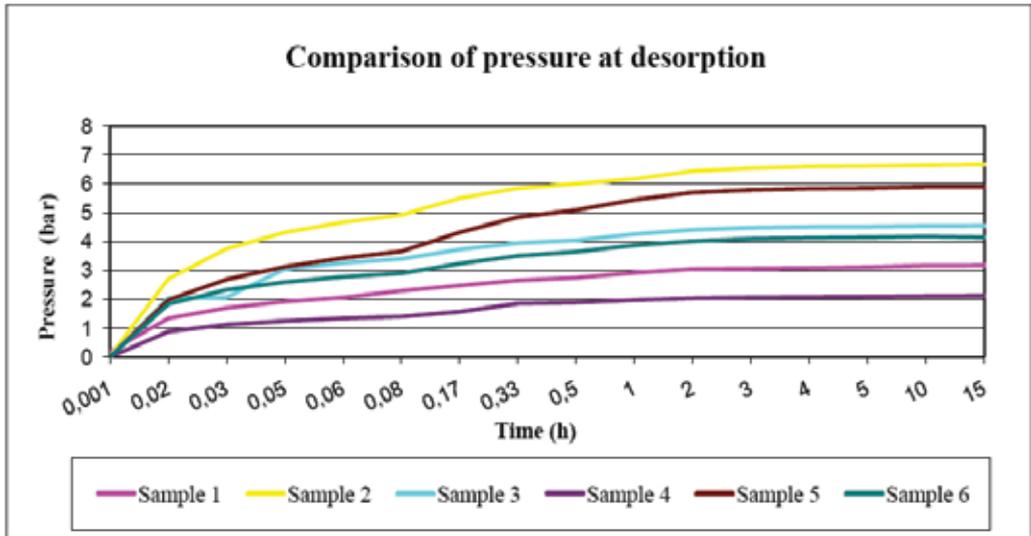
Figure 12. Pressure increase in autoclave during desorption of gas from the 1 to 6 samples.

Also in these two cases the additional N_2 pressure caused initially a slight decrease of the total pressure at both samples, but then the pressure started to rise and it reached the value of 95.13 bar for sample 2-1 and 94.38 bar for sample 5-1, respectively. Sample 2-1 released 10.02 bar of gas or 18.25 g/kg, and sample 5-1 released 10.03 bar of gas or 18.78 g/kg. As the proportion of adsorption is considerably higher than for other samples, also the proportion of desorption will be higher. Desorption of the sample 2-1 equals 12.09 g/kg or 44.40 %, and of the sample 5-1 10.74 g/kg or 37.58 %.

Third set of measurements
With the intention to explain the appearance of the newly arisen P_x of gas, we

have sampled the gas for analysis from autoclave during the adsorption process. During each sorption process, the gas components were sampled twice - by **sampling A** (at the end of the second step of adsorption of CO_2 - i.e. after 90 min), and **sampling B** (after dosing by N_2, just before desorption) (see also chapter about sampling of gas components). Into a piston ampoule, one bar of gas sample was taken. Results of gas composition of the A and B samplings in the case of samples 2-1 and sample 2-2 (in fact two parts of the same lignite lithotype) are presented in Table 6.

In all cases of the type A sampling, the gas analysis resulted to more than 90 % of CO_2 (in the case of 2-1 in Ta-

Table 6. Gas composition of sampling A and B during sorption of a gelified fine detrital lignite (fD90 G10) sample duplicates 2-1 and 2-2. Time of sampling, temperature and pressure in autoclave are given for complete information.

Sample	Composition	Sampling	t/h	T/K	P/bar/	Gas sample composition, φ/%				
						CH4	N2	O2	CO2	Ar
2-1	fD 90 % G 10 %	A	1.5	295.9	(P_3) 58.6	0.1	1.1	0.7	98.2	0
		B	6	294.4	(P_x) 90.7	1.5	67.2	0.9	30.1	0.4
2-2	fD 90 % G 10 %	A	1.5	296.4	(P_3) 58.0	0.3	2.5	0.6	96.6	0
		B	6	295.9	(P_x) 95.6	0.2	69.0	0.3	30.2	0.4

ble 6 even more than 95 %), and the remaining 10 % of CH_4, N_2 and O_2. In the case of the type B sampling the gas analysis resulted (Table 6) to more than 60 % of N_2, around 30 % of CO_2, and the rest represented by CH_4, N_2, O_2 and Ar. Minimal amounts of the last two gases appear owing to presence of air in the dosing pipes. The CH_4 is the residue from the coal matrix.

In the procedure, the proportion of the added N_2 pressure reached only around 30 % of the total pressure. Gas analysis resulted into around 60 % of N_2.

Regarding these results it can be inferred that the additional N_2 overpressure caused CO_2 compression and consequently condensation. Instead of 30 % N_2 as much as 60 % (i.e. ca. two times more) of N_2 could be dosed on account of CO_2 compression.

Results of gas analysis permit to explain the reasons for appearance of the newly arisen P_x pressure after the third dosing step in the confined system. It can be affirmed that 10 bar were released from the sample's structure, as two times more N_2 gas than supposed entered the system.

DISCUSSION

Experience with coal mining and coal dust and gas outbursts so far (e.g. overview in LIKAR (1995); and references there-in) indicates that these events are connected to a considerable degree to occurrences of masses of fine detrital lignite varieties, especially if the lignite is gelified (MARKIČ et al. (2001)). On the laboratory level, an outstanding gas proneness of the fine detrital gelified lignite variety was already ascertained by several studies, such as those of ZAPUŠEK & HOČEVAR (1998), LIKAR (1999), PEZDIČ et al. (1999a,b), ZAVŠEK (2004), LIKAR et al. (2008).

1. We established a measurement system on the modernized apparatus

and improved the volumetric method (Pezdič et al. (1999b), Dobnikar (2003), Mihelčič (2004)). We also improved the gas sampling from reaction cell during sorption simulation progression.

When updating the device, we acquired a new factor in the sorption process through monitoring the temperature of temperature sensors (T_{system}, $T_{environment}$). This is very important as it affects all other parameters involved in sorption process. The net volume of the reaction container has been changed, the sound for pressure change measurements has been moved closer to autoclave and the volume reduced with the valve (V).

2. Comparable adsorption/desorption investigations were performed on various lignite lithotypes. High pressure measurements of adsorption and desorption were done on six samples varying in their lithotype composition. Owing to the size of autoclave opening the lignite samples had to be correspondingly prepared. We simplified the sample preparation using grinding in the grinder and sowing on sieves with aperture 2−4 mm.

Sorption measurements progressed in a reaction cell (autoclave) where we kept a lignite sample. The sample has been loaded in two steps with CO_2 (up to 60 bar) and in the third step with N_2 (up to 85 bar). Measurement for determination of moisture's impact on sorption were done. Measurements results show sorption's dependence on moisture content as sorption increases regarding increased moisture content in the sample. All measurements show that in the second adsorption step much less gas is adsorbed as in the first step (Figure 10).

The most CO_2 gas was adsorbed, in the first two steps, in the samples 2, 5 and 6. (Figure 10). Second adsorption step adsorbed only around half or 50 % amount of adsorbed gas in the first step. The comparative amounts of measured adsorption (first plus second step) indicate the dependence of the amount of adsorption upon the sample lithotype. Samples higher in contents of fine detric matrix tend to adsorb more gas (Figure 9).

Comparative adsorption values (Figure 11) of the first and the second CO_2 dosage and of the N_2 overpressure value show differences owing to different lithotype composition of samples. Major deviations between curves are seen at the third N_2 loading step when after the initial pressure decrease the curve starts to rise (pressure rises), and reaches around (+10 bar) after six hours.

The newly arosen (P_x) pressure, appearing after the third dosing stage

in the confined system, is explicit and means a considerable loading of the firm coal's skeleton.

The comparative desorption readings (Figure 12) show pressure changes during desorption. Desorption depends on the proportion of adsorption in the first two stages and on released gas in the third stage. The lowest measured desorption value after 15 hours is shown for the 4-1 sample. This sample is the most heterogeneous (X 80 %, cD 10 %, fD 10 %), and the desorption value is 2.12 bar. The highest measured desorption value after 15 hours shows the 2-1 sample. This sample comes from a fault zone (fD 90 %, G 10 %), and it desorption value is 6.67 bar.

3. Of the key importance was also the sampling of gas in autoclave. Gas analysis showed that at N_2 dosing in autoclave a high compression of CO_2 was achieved. When in the third step 30 bar of N_2 was dosed, the gas ration in autoclave should have been 2 : 1 in favour of CO_2. Chemical analysis proved the achievement of compression, but the achieved ratio of gases was reversed, 1 : 2 in favour of N_2.

4. After addition of the N_2 pressure, the adsorption tests for all samples showed first a slight initial decrease of total pressure (from 1.70 to 4.19 bar) - that means an instant gas adsorption into the lignite matter - and then the pressure increase - this means release of gas out from the lignite matter (for an example see Figures 2, 7; whereas data for all samples are in ŽULA, (2006)). After six hours, the pressure reached the maximal value, while temperature decreased markedly, for almost 5 °C (Figure 2 - upper graph). This phenomenon indicates that the coal samples were additionally affected owing to P_x of the gas. The P_x pressure can be related to the conditions in mine. During advanced exploitation of lignite by the longwall working face method (longwalls being ca 100 m wide and 4 m high, with additional vertical concentration of excavation), substantial deformations and (differentially) increased pressures occur ahead of the longwall faces. These factors have an impact on strength of the lignite's skeleton (ZAVŠEK, 2004), and may lead in some extreme situations to coal and gas outbursts.

5. In the further research, more accent should be put on influence of temperature and moisture on sorption. Owing to influence of environment temperature on temperature changes in autoclave, the autoclave will have to be insulated. Planned is also a new concept of reaction vessel with a wider input opening

to allow passing of larger coal fragments. With this also dosing tubes will have to be enlarged to permit faster gas input. Measurements will be supplemented with additional gas mixtures of varying ratios of CO_2, CH_4 and N_2 Sorption properties of lignites will be shown with isotherms. Micropetrographic description of samples will be supplemented with the scanning electron microscopy (SEM).

CONCLUSION

From these reasons, to clarify gas sorption characteristics of the Velenje lignite and to supplement previous investigations with some new aspects, gas sorption tests on different lithotypes at different laboratory (autoclave) conditions of dosing gases, pressures and moistures have been studied in the experimental work which is presented in this paper. The main conclusions of our work, starting with some technical improvements, are cited below:

1. The methodology of adsorption/desorption was tested on various lignite lithotypes by introducing additional parameters (temperature, moisture, speed of dosing). Upgraded was the hardware and software of the sorption research system as originally described by Žula (2006), Pezdič et al. (2008–2009). As during dosing the adsorption (amount of adsorbed gas) cannot be measured, it was important that we accelerated the speed of dosing. The dosing time of 3−5 s was achieved, although the entire adsorption process has not yet been properly registered.

Modernization of software makes detection of the signal more accurate as it is read each second assuring to capture the most important data in the first minute after dosage when the adsorption is maximal.

2. Desorption depends on the adsorption share in the first two steps, on the compressed CO_2 gas in the third steps, and on the gas mixture release velocity when the pressure was decreased to one bar.

The lowest measured desorption value after 15 hours was shown by the 4-1 sample (by composition the most heterogeneous sample), namely 2.12 bar or 3.74 g/kg, and the highest value the 2-1 sample (from fault zone), namely 6.67 bar or 12.09 g/kg.

Samples with fine detrite (Samples 2, 5, and 6) adsorbed the highest amounts of gas. The best result of sorption was achieved with sample 2 (fine detrite from foult zone) which adsorbed 27.23 g/kg of gas and desorbed 12.09 g/kg respectively 44.4 % adsorption.

3. The sorption methodology is still in the development phase. The principal future research trends will be aimed at collecting new data on coal petrology, calculation of bulk coal sorptive capacities and perfecting the mechanical gaseous mathematical model of the lignite - gas system. Results from sorption tests will be used to verify and fit the mentioned mathematical model which is being developed in the last few years in order to study the influence of structural and petrographical changes of the Velenje lignite depending on various stress states and presence of gases.

Acknowledgements

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