Sorption behaviour of methane and carbon dioxide on bituminous coal

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Introduction

The fundamental requirement for the future of the coal energetic sector in the Czech Republic is to reduce the CO_2 emissions from the combustion processes, what should be achieved by increase of their utilization or by CO_2 recovery, utilization or injection into suitable geological structures. One of the prospective methods is to utilize the recovered CO_2 from the power production for coal bed methane extraction from the unexploited bituminous coal seams.

The North Moravian region is well known for its bituminous coal deposits, a part of which is unexploitable, but it contains a substantial amount of coal bed methane, therefore investigation of CO_2 and CH_4 sorption at laboratory scale has been of a primary interest as a support for the ECBMR (Enhanced Coal Bed Methane Recovery) developing technology.

PART I. Carbon dioxide and methane sorption capacity of bituminous coal from North Moravian region

The study has been carried out on one sample of high volatile bituminous coal (4), four samples of medium volatile bituminous coals (1,3,5,6) and one sample of low volatile bituminous coal (2) with variable to high contents of vitrinite and inertinite. Their basic characteristics are given in Table 1.

For the estimation of sorption capacity for carbon dioxide and methane amount occluded in coal the theoretical isotherms were constructed according to the previously published method (Fuel 1998, 77, 71-76). The isotherms are shown in Figures 1-6.

Table 1 Characterization of coal samples

Sample	1	2	3	4	5	6
Mine	DPB	PÚ Václavovice	PÚ Václavovice	Trojanovice	Trojanovice	Trojanovice
Borehole	DP-1	VA -1H Datyně	VA -1H Datyně	TR-2 Frenštát	TR-2 Frenštát	TR-2 Frenštát
Depth [m]	1138.0-1139.0	1096.2-1097.0	664.2-664.6	1061.5-1062.0	1109.2-1109.6	1236.8-1240.2
W^a [%]	0.9	0.6	0.7	1.4	1.0	0.6
A^d [%]	6.8	5.6	8.9	2.5	1.3	6.4
V^{daf} [%]	28.6	20.5	29.1	33.6	26.2	30.0
Swelling index	6	9	8	8,5	1	4,5
Calorific value [MJ/kg]	35.066	36.472	35.799	35.255	37.350	35.888
R_o [%]	1.05	1.40	1.10	0.81	1.02	1.00
V [%]	52	76	69	60	11	53
L [%]	7	0	12	11	21	16
I [%]	41	24	19	29	68	31

W^a – analytical water, A^d – ash (dry basis), V^{daf} – volatile matter (dry and ash free basis), R_o – reflectance, V – vitrinite, L – liptinite, I – inertinite

Figs.1-6 Comparison of sorption capacity of samples 1-6 for CO_2 and CH_4
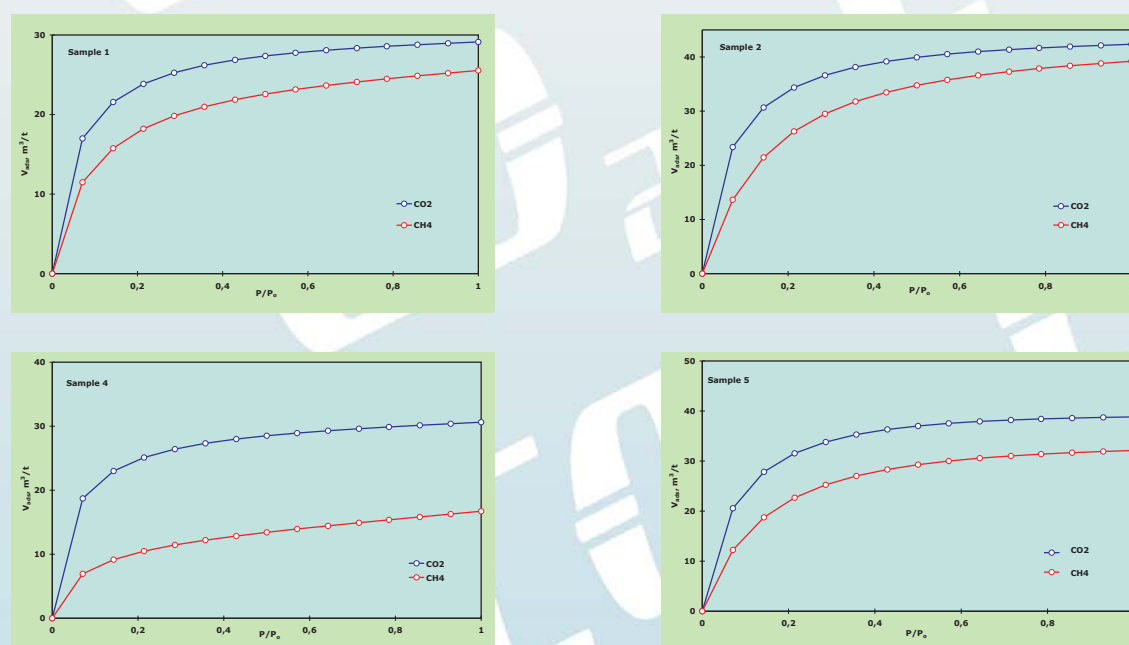
From the course of the isotherms it is obvious, that the tested coals adsorb more carbon dioxide than methane and the ratio $CO_2 : CH_4$ ranges from 1.1 to 2.3 however the dependence on rank is not evident. From the results given in Table 2 it follows that the dominant part of gas is bound in micropores.

Table 2 Parameters of porous structure according to CH_4 and CO_2 sorption and their sorbed volumes

Sample	V_{mm} [cm³/g]	V_{micro} [cm³/g]		$V_{mm+micro}$ [cm³/g]		$V_{ads, micro}$ [cm³/g]		$V_{ads, total}$ [cm³/g]		Ratio $CO_2 : CH_4$
		CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	
1	0.036	0.090	0.057	0.126	0.093	20.2	25.7	25.5	29.13	1.1 : 1
2	0.042	0.147	0.085	0.189	0.127	33.1	38.4	39.2	42.4	1.1 : 1
3	0.033	0.063	0.078	0.096	0.111	14.2	35.4	19.6	38.3	2 : 1
4	0.049	0.042	0.057	0.091	0.060	9.4	25.9	16.7	30.6	1.8 : 1
5	0.021	0.130	0.082	0.151	0.103	29.4	37.2	32.1	38.8	1.2 : 1
6	0.021	0.045	0.064	0.066	0.109	10.1	29.1	12.8	30.8	2.3 : 1

V_{mm} - volume of meso- and macropores according to Hg porosimetry, V_{micro} – volume of micropores and
$V_{mm+micro}$ – volume of meso-, macro- and micropores, $V_{ads, micro}$ – volume of CH_4 a CO_2 sorbed in micropores,
$V_{ads, total}$ – total sorbed volume of CH_4 a CO_2 (including gas in the free space of meso-and macropores)

PART II. The differences between kinetics behaviour of carbon dioxide and methane in dependence on temperature and pressure

Sorption measurements were carried out using an Intelligent Gravimetric Analyser (IGA 002) Hiden Analytical (Fig. 11).

The sample No.3 was selected for the kinetics experiment. Under the calculation (Fig.3, Tab.2.) the sample had approximately two times higher sorption affinity for CO_2 than for CH_4. It confirmed its suitable sorption capacity for CO_2.

On Figs.7-10, there were recorded kinetics curves of two pressure sets 0.0-0.1; 0.3-0.4 MPa at the temperatures 25 and 45 °C of CO_2 and CH_4.
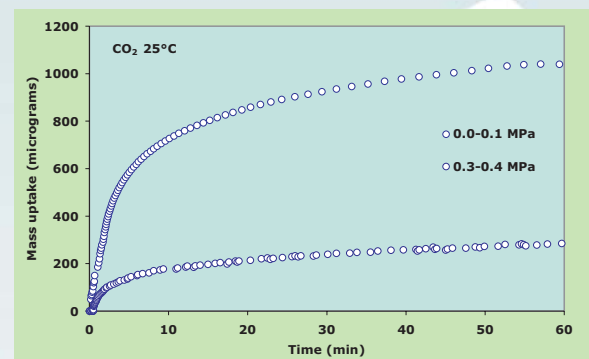

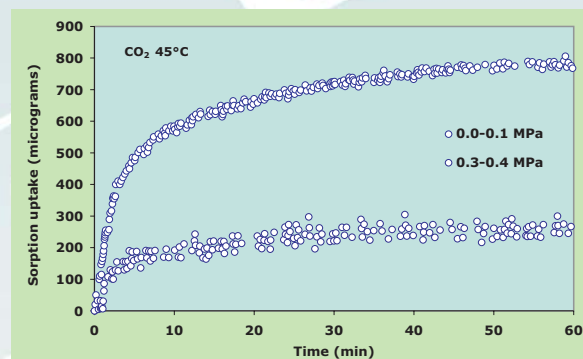Fig.7 CO_2 mass relaxation at pressure ranges 0.0-0.1; 0.3-0.4 MPa at 25°C

Fig.8 CO_2 mass relaxation at pressure ranges 0.0-0.1; 0.3-0.4 MPa at 45°C
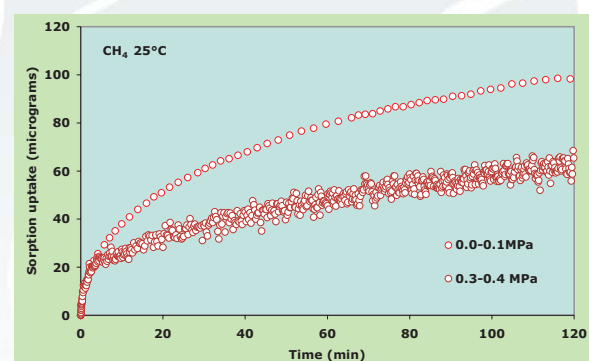
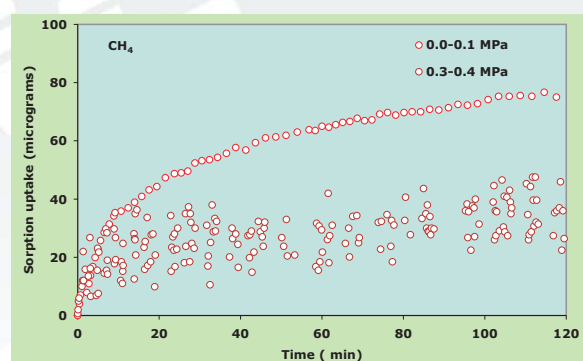Fig.9 CH_4 mass relaxation at pressure ranges 0.0-0.1; 0.3-0.4 MPa at 25°C

Fig.10 CH_4 mass relaxation at pressure ranges 0.0-0.1; 0.3-0.4 MPa at 45°C

Fig.11 Gravimetric sorption analyzer IGA 002 HIDEN

Measurement conditions

Grain size	< 0.2 mm
Sample weight	0.1 g
Outgas conditions	temperature 105° C under vacuum 10^{-6} Pa up to constant weight
Gas	CO_2, CH_4
Run mode	isotherm
Temperature	25, 45° C
Final pressure	1 bar, 4 bar

Weighing resolution – 0.2 µg
Accuracy of constant pressure – ± 0.02 %
Accuracy of temperature – ± 0.05 °C

The apparatus registers continually the sorption kinetics at each pressure point in detail and records for individual pressure steps a real time of equilibration.

The computer calculates an actual time, which corresponds to reaching 98% of the theoretical value for the equilibrium sorption.

The temperature at CH_4 sorption (Figs. 9,10) has not played such an important role and the influence of the pressure was more significant. On the other hand the temperature has played an important role in the process of the CO_2 sorption (Figs. 7,8) which was multiplied by the pressure increasing.
The negative roles of the temperature and pressure increase were displayed at the gases equilibrium state.