



Influence of Temperature on Sorption of Carbon Dioxide in Coals

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Summary

The paper summarizes the experimental results of carbon dioxide sorption process on selected coal samples from Polish mines having different texture and maceral composition, in the context of CO₂ sequestration.

In order to examine the temperature dependence of sorption process and heat effects accompanying interactions of the mine gases with coal matrix, the sorption experiments were made at several temperatures using volumetric method.

Furthermore, the analysis of equilibrium isotherms allowed to estimate thermodynamic parameters, i.e., isosteric heat of sorption as a function of coverage, for all coal-gas systems. From a technological point of view, the conditions in which heat exchange takes place during sorption phenomenon (under various coal reservoir conditions) become significant. This last factor also determines the intensity of gas emission (the diffusion rate) and, in consequence, the unexpected unseal of coalbed followed by the changes in the bed permeability.

Keywords: coal, isosteric heat of sorption, CO₂ sequestration

Introduction

The development of industrial production causes permanent increase in atmospheric CO₂ pollution as a result of the combustion of fossil fuels. Based on rank classification of coals, Anthracite is a harder coal, containing from 91% to 98% fixed carbon, the least of hydrogen content, when bituminous coal can be contain fixed carbon between 69 and 86 percentage. In turn, brown coal, is a very soft, contains up to 70% water and emits more pollution than other coals.

The sequestration of CO₂ in coalbed is seen as a possible method to reduce CO₂ emissions in atmosphere. In this respect, the sorption/desorption research, among the many experimental methods, play a special role to extend knowledge about the accumulation and behaviour of mine gases within the coalbeds, especially in the aspect of storage problem, and in connection with the phenomena of instantaneous outbursts of a mass of rocks and gases (Beamish et al. 1995). The mechanism of these processes is still unresolved.

It is well known that, the injected carbon dioxide (ECBM technology), would be disposed into porous and permeable coal reservoirs, covered with a low permeability seal, at depth around 800-1000 meters, where the CO₂ will be in a dense phase than gas phase. The process of gas deposition in coal beds should be carried out under conditions guaranteeing long-term stability of the reservoir system. Much of the CO₂ will be stored in micropores or dissolved in the water of the coal reservoir. At the same times, CO₂ injection into the coalbeds improves the methane recovery, which proceeds by desorption from the coal. For all these reasons the question of predicting the

sorption (storage) capacity in given coalbed, based on the sorptive and also diffusive properties of coal sorbent, is important.

Carbon dioxide and methane are present practically in all coalbeds, as a gases deposited in its structure. The amounts of gases are to a great extent, controlled by pressure, temperature (changing with the depth), humidity and geological time (Clayton 1998).

Apart from the temperature and pressure conditions in laboratory experiments under study, the sorption capacity in coals is determined by the important factors; rank of coals, maceral composition, moisture content, ash content (van Krevelen 1993, Bustin and Clarkson 1998, Mastalerz et al. 2004).

The coal-gas system is also of interest from a theoretical point of view, since the intermolecular forces involved are not relatively simple to model (the complex structure of pores, petrographic composition, chemistry of coal surface). Thus, investigations of heat (energy) exchange that take place during sorption phenomena to make an estimate the qualitative and quantitative characteristics of interactions between gas molecule and sorbent surface (Young and Crowell 1968). Up to now, there is still no clear understanding of the interactions between mine gases (CO₂, CH₄) and coal surface.

In order to determine the heat effect of sorption, the calorimetric, chromatographic, and the isosteric methods are used the most frequently. Gas chromatography is recommended most often for simple sorption systems, i.e. those with Henry's isotherm. The calorimetric method, on the other hand, yields the best results in the range of low coverage, but this method may be prone to systematic errors, due to failure to

meet the thermodynamic equilibrium condition (especially for coal-gas systems). Satisfactory results may be obtained using the isosteric method, when the heat values of sorption are estimated from the experimental data in thermodynamic equilibrium. It should be worth noting, that this approach is valid for an ideal gas, i.e. for low pressures range and in experimental conditions provided that the minimum gas-phase volume to volume of sorption phase ratio (Young and Crowell 1968). Hence, this method is limited to sorbents that are assumed to be inert (for example, not swelling) during a sorption process. It must be emphasized, that some caution is needed for the higher pressures investigations.

Up to now, these phenomena have not been completely explained. The basis for their description are the results of sorption/desorption experiments in the system: single gas – coal.

A studies of CO₂ sorption on selected coals from Polish coal mines are presented. The main aim of this work was to discuss the energetic effects given by isosteric heat of sorption at very low pressures (very low surface coverage) and their dependence on the different characteristics of coal. These investigations

contribute to better understanding of the interaction of carbon dioxide molecules with coal matrix in the aspect of CO₂ behaviour in coalbed and gas storage problem.

Experimental

In this study, the volumetric method was used to measure carbon dioxide sorption. The measurements were carried out on the degassed coal samples (up to pressure 10⁻³ Pa), in the range of pressures up to 0.1 MPa.

The equilibrium isotherms were determined at three temperatures (293, 298 and 303K). This method is time consuming to determine all data (due to repetition of the measurements at various temperatures). All experiments were performed below the critical temperatures and pressure of sorbate (that is 304 K and 7.38 MPa), thereby maintaining vapour-state conditions.

The sorption investigations included three coals with the characteristics presented in Tables 1 and 2 (chemical, technological and petrographic characteristics). Selected fractions with 0.5-0.75 mm of coal grains were used for the measurements.

Tab. 1 Selected characteristics of the examined coals
Tab. 1 Wybrane charakterystyki badanych węgla kamiennych

Sample	C ^{daf} (%)	V ^{daf} (%)	A ^d (%)	(O+N) _d ^{daf} (%)	V _o · 10 ² (cm ³ · g ⁻¹)	V _{mac} · 10 ² (cm ³ · g ⁻¹)
Coal 1	92.1	8.53	9.10	3.75	7.30	1.02
Coal 2	87.6	27.87	7.78	6.40	5.50	2.09
Coal 3	82.0	36.86	8.09	12.02	5.02	2.33

V_o – total pore volume determined from densimetric measurements

V_{mac} – determined from mercury porosimetry

Subscripts
a – analytical state,
d – dry coal basis,
daf – dry ash-free

Tab. 2 Petrographic analysis of the examined coals
Tab. 2 Analiza petrograficzna próbek węgla kamiennego.

Sample	Group of macerals (vol %)			
	Vitrinite	Inertinite	Liptinite	Mineral Matter
Coal 1	83.5	14.5	0	2.0
Coal 2	82.2	16.7	0.7	0.4
Coal 3	84.1	9.8	3.2	2.9

Discussion and results

Coal is microporous solid with a developed internal surface, able to sorb the gases.

The coal samples selected for this study, presents various type of coal. They have a wide range of Volatile Matter content (Vdaf, from 8.53 to 38.86). Next, the coal samples are dominated by vitrinite group macerals. There is also a good correlation between vitrinite reflectance values (R_o , coal 1 – 2.18 %vol, coal 2 – 0.95 % vol, coal 3 – 0.80) and carbon content.

These three coals differed significantly in their sorption (storage) capacity with regard to CO_2 . As expected, the experimental results performed with the same coal grain size, indicated a distinct effect of rank (Bustin and Clarkson 1998, Marecka 2007). There is significant correlation between the level of carbon content within whole coal sample and its gas sorption ability. The sorption capacity of coal 3 with the highest volatile part was distinctly lower. In the pressure – temperature conditions under study, the CO_2 capacity of this coal did not exceed $2.0 \text{ cm}^3 \text{ STP } CO_2/\text{g}$ coal. However, this capacity may not be realized in water saturated and constrained coal seams, as was be discussed in paper (Krooss et al. 2002).

Moreover, the sorption of CO_2 for anthracite type of coal 1 with a slightly higher total volume of pores and porosity, and characterized by higher content of carbon was the highest. It is suggested that, the pores of low rank coal are very narrow or more closed than the anthracite ones.

The gas sorption data show a linear increase of sorption capacity with rank, in good correlation with literature data (Beamish et al. 1995, Crosdale et al. 1998, White et al. 2005). In contrary, Krooss (2002) has been found, only weak this correlation with respect to the rank, in some cases of coals.

It is usually reported that, the equilibrium sorption of a single gas is described by its isotherm and heat of sorption. Among them, the influence of temperature upon the sorption process is the most important subjects of the study. In this aspect, the experimental results, are reported as the set of three sorption isotherms for all gas-coal systems.

From the figure 1 (as an example), it can be observed that the effect of increasing temperature is to decrease the sorption capacity of the coal sample. However, differences between sorption capacities is not too large with temperature.

Heat of sorption is an important thermodynamic parameter for sorption-thermodynamic studies. This is also parameter of interest due to increasing relevance of sorption/desorption processes for gases storage. In this study attention was focused on the heat effects accompanying interactions of the carbon dioxide with coal matrix. Carbon dioxide molecule is linear and has a high quadrupole moment which should be result in higher energy of these interactions. Basing on the sorption isotherms obtained at three different temperatures, the isosteric heat values of sorption (q_{st}), were estimated using the Clausius-Clapeyron

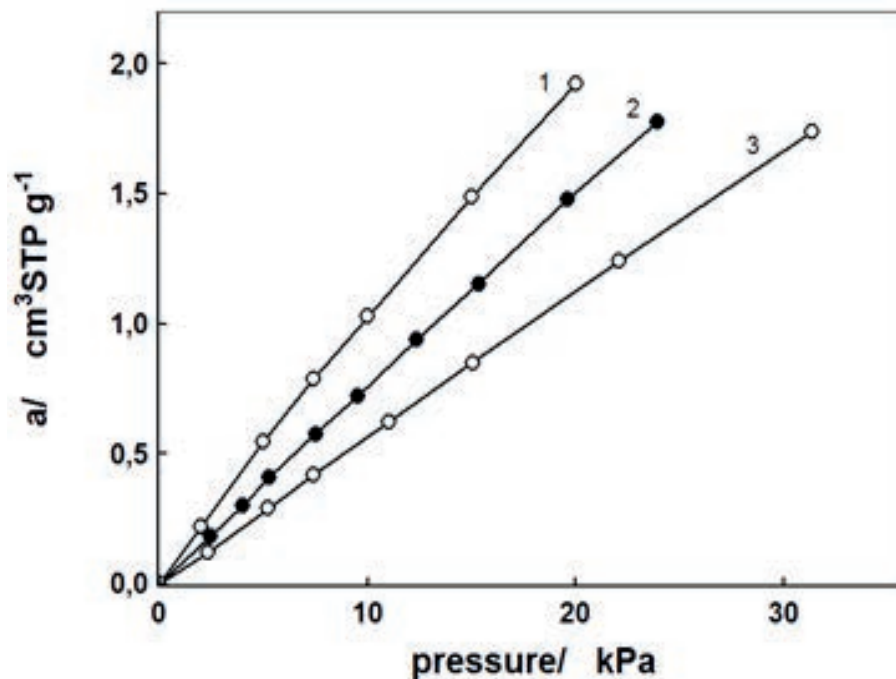


Fig.1 Sorption isotherms on coal 3 at (1) 293 K; (2) 298 K; (3) 303 K.

Rys. 1 Izotermie sorpcji CO_2 dla węgla kamiennego 3, wyznaczone w temperaturach: (1) – 293 K, (2) – 298 K, (3) – 303 K.

equation (Young and Crowell 1968):

$$q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_a$$

where:

- a- amount of the gas sorbed,
- p - equilibrium pressure,
- R-gas constant,
- T-temperature.

Summary results of calculations are shown in Table 3.

As can be noticed, temperature dependences are diminishing - with the increase of the amounts of the sorbed CO₂, the values of heat of sorption decrease, but they are still higher than the heat of carbon dioxide condensation (16.7 kJ/mol). This can lead to the conclusion that the nature of energetic interactions between this gas molecules and coal surface is physical. Comparable results have been reported in the literature. Furthermore, the resulting heat of sorption reveal a some differences between the coals, as shown in Table 3. Additionally, the differences are slightly pronounced at the beginning of the sorption phenomena. For example, the effect of increasing CO₂ sorption on the isosteric heat of sorption on coal 1 is small, about 3 kJ/mole. That, stronger interactions of CO₂ molecules with surface may enhance the sorption, followed by increases the capacity at very low pressures suggesting a contribution from sorption in

molecular size micropores. This is typical in the case of weaker interaction due to the hydrophobic nature of high rank of coal.

The values of q_{st}^o , chosen so that $a \rightarrow 0$, characterize direct interactions between the sorbate molecules and the coal surface at very low pressures, which are equal to: coal 1 - $q_{st}^o = 41.80 \text{ kJ}\cdot\text{mol}^{-1}$, coal 2 - $q_{st}^o = 43.10 \text{ kJ}\cdot\text{mol}^{-1}$, coal 3 - $q_{st}^o = 48.09 \text{ kJ}\cdot\text{mol}^{-1}$, respectively.

Taking to the consideration the coal 3 with the low inertinite content, the highest heat of sorption is observed for this low rank coal, most probably caused by the sorption in narrowed micropores (molecular size) being inaccessible one. This fact correlates with their lower CO₂ sorption capacity, in contrary to other coal samples. CO₂ sorption on coal 2 follows a very similar energetic pattern q_{st} versus coverage. These values found are of a decreasing trend, i.e., by increasing sorption, q_{st} values decrease. Sample of coal 2 contains the most varied maceral composition and low volume of micropores.

Moreover, observed pattern of temperature dependence for high rank coal, with the highest C^{daf} and the lowest V^{daf} , when compared with other coal samples, is associated with more ordered structure (crystalline-like domains) and more homogeneous (chemical) surface of coal 1. The sorption in the higher oriented coal case, takes place mainly by the dispersion component of the van der Waals forces.

A conclusion can be drawn that, the interactions

Tab. 3 Isosteric heats of CO₂ sorption on tested coals, in temperature range 293-303 K

Tab. 3 Izosteryczne ciepła sorpcji CO₂ na badanych węglach kamiennych, wyznaczone w zakresie temperatur 293 K - 303 K.

a [cm ³ STP·g ⁻¹]	Q _{st} [kJ·mol ⁻¹]		
	Coal 1	Coal 2	Coal 3
0.08	40.30	42.50	47.48
0.10	39.00	41.85	46.99
0.12	38.00	41.20	46.70
0.16	37.26	40.30	46.10
0.20	37.01	39.7	45.50
0.24	37.00	39.30	45.04
0.28	36.90	38.76	44.69
0.34	36.80	38.64	44.02
0.38	36.86	38.50	43.95

between the microporous structure of coal sorbent and gas molecules are dominant, in first contact. In other hand, it was also observed that the limiting value of sorption heats decreased with increasing the surface oxygen compound in coals (Table 1).

It should be remembered that coal is a sorbent with a very complex structure and interpretation of equilibrium experimental data and sorption heats with respect to CO₂ and other sorbates still presents a major difficulty (White et al. 2005). For instance, a gas sorption is highly dependent on coal rank and petrographic compositions (Mastalerz et al. 2004). There is no clear understanding on the possible interactions in coal – gas systems in the aspect of correlation between the key parameters (Beamish et al. 1995, Mastalerz et al. 2004). Moreover, at high pressures of sorbate (above one atmosphere), as the amount sorbed of carbon dioxide increase, these interactions becomes more and more complicated, because they could slightly change the coal structure (due to CO₂ penetration therein coal material) and hence much higher (and sometimes underestimated) capacities, may have affected the results obtained (Karacan 2009). But, at low pressures range of carbon dioxide, the coal swelling process involved is absent.

It is supposed from a literature and this work, that although in surface phenomena porous structure of coal sorbent is very important, the role of coal surface chemistry may be also crucial, but the latter is not yet recognized. It is just this aspect of coal features which makes them interesting for investigations of energetic effects by sorption of carbon dioxide. Hence, a better understanding of the interaction between CO₂ molecules and coal matrix is needed.

Another reason for studying different aspects of gas sorption on coal are gases and rocks outbursts. From a technological point of view, the conditions in which heat exchange takes place during sorption phenomenon, become significant. In the recent years, Nodzeński (1968) reported in relation to calculated heat of sorption and in connection with a non-isothermal model of process, that during liberation of methane, the temperature inside of a coal will be decrease, especially, if the process occurs under conditions where heat exchange with the surroundings will be difficult. Under real conditions, in situ, this fact will be determined the intensity of gas emission and, the unexpected unseal of coalbed, introduced by energetic interactions of gas molecules and coal and the amount

of desorbing gas. These must be taken into account when considering gas recovery or CO₂ sequestration. It is worth note however that, the injection of CO₂ in coalbed possibly can be reduce the risk of outburst process.

Conclusions

In recent years, the capture and the underground storage of carbon dioxide have been considered as an option for reducing greenhouse gas emissions. In this context, the influence of the rank and hence also of the porous structure on the sorption properties was studied by means of CO₂. The essential problem in these processes are the sorption interactions of carbon dioxide molecules with coal surface. The clear understanding of CO₂ behaviour in coal sorption system is still insufficient.

Special interest of this work is the temperature dependence of sorption process. A set of three coal samples from Polish mines were chosen to analyze sorption capacity and isosteric heat of sorption (q_{st}) by using the Clausius-Clapeyron equation. The following conclusions can be drawn from the study:

Experimental data confirm good penetration of carbon dioxide. CO₂ sequestration will can be stored in the coalbed in an sorbed state within the micropores. The isotherms analysis shown the anthracite coal sorption capacity as the highest for very low pressures and ambient temperatures.

Variation of q_{st} values with surface coverage found are of the decreasing trend, i.e., by increasing sorption amount on coal, isosteric heat of sorption values decrease, because of the effect of heterogeneity of coal surface. It is suggested that the narrow micropores (of molecular size) can be enhanced the interactions between CO₂ molecules and coal surface at very low coverages (and at very low pressures). The highest values of q_{st} was found for low rank coal with low content of inertinite.

It seem reasonable to believe that the crucial factors are difference in the structure of pores of coals and the contribution of the various groups of maceral, in physicochemical interactions like sorption phenomena.

Acknowledgements

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Streszczenie

Praca prezentuje wyniki badań sorpcji CO₂ na wybranych próbkach węgla kamiennego (o zróżnicowanej teksturze i różnym składzie macerałów) z polskich kopalń, w aspekcie problematyki związanej z sekwestracją ditlenku węgla.

Celem pracy było określenie wpływu temperatury na sorpcję tego gazu oraz efektów cieplnych towarzyszących wzajemnemu oddziaływaniu gazów kopalnianych z powierzchnią matrycy węglowej.

Przeprowadzona została analiza izoterm sorpcji uzyskanych metodą objętościową w kilku temperaturach, dla każdego układu węgiel kamienny-gaz, co stanowiło podstawę do wyznaczenia izosterycznego ciepła sorpcji (wielkości termodynamicznej) w funkcji zapęnlania powierzchni.

Z technicznego punktu widzenia, istotne znaczenie mogą mieć warunki, w których wystąpi przepływ ciepła spowodowany zjawiskami sorpcyjnymi (w różnych uwarunkowaniach zbiornika w wyrobisku węglowym). Można przewidywać, że warunki te będą określać intensywność emisji gazu (szybkość jego dyfuzji), co w konsekwencji może prowadzić do rozszczelnienia złoża węglowego oraz zmiany jego przepuszczalności względem gazu.

Słowa kluczowe: węgiel kamienny, izosteryczne ciepło sorpcji, sekwestracja CO₂