Methane and Carbon Dioxide Sorption Kinetics in Polish Coals

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Summary

Experimental investigations of methane and carbon dioxide sorption kinetics were undertaken because of the gas capture and storage problems. Classical volumetric method, in isothermal-isobaric conditions, was applied.

The main aim of the studies was to show an influence of the rank (chemical and petrographic composition) and hence also of the porous structure on the kinetics properties of coals. The results for different type of coals from Polish mines were compared.

The kinetic sorption experiments can provide data for the prediction of the efficiency of gas storage (sorption) in coal beds. This subject has also become especially interesting in recent years with regard to the concept of CO_2 sequestration in underground geological formations (ECBM technology), in unmineable coal beds.

Keywords: coal, sorption kinetics, CO_2 sequestration

Introduction

Greenhouse Gases in the atmosphere, especially the carbon dioxide, has become the main reason of change of global climate, chiefly as a results of fossil fuel combustion. The application of Capture and Storage (CCS) technique can reduce the carbon dioxide emissions about 50–60%. Coal beds that are not mined and empty natural gas reservoirs can be potential locations for CO_2 long-term storage. This technology is therefore very promising.

The idea of the geological sequestration into deep coal structures is described as capturing CO_2 and depositing it in deep underground coal beds. In addition, the enhanced coalbed-methane (ECBM) technique combines exploitation of methane from coal beds with storage of carbon dioxide. Injection of CO_2 allows for intensification of methane recovery. The model of fluid flow in coal bed show that the efficiency of this technique depends on the CO_2 diffusive transport rate from the fractures (macrocleats), to the coal matrix with molecular dimensions of pores. The CO_2 will sorb on the coal surface in selective sorption process and will cause desorption of methane (releasing in a natural way in underground conditions of temperature and pressure). However, the sorption system: natural coal-gas, is a very complex for the complexity of the physico-chemical properties of coal which changing from seam to seam, its porous structure as well as the involved character of the sorption process itself. For example, sorption of carbon dioxide caused a swelling and shrinkage (deformation) of coal matrix as well as reduction of coal porosity and permeability (Larsen 2004, Karacan 2007, Mazumder 2008). The higher the pressure, the more CO_2 can be sorbed and the more the coal should swell. Nevertheless, Clarkson and Bustin (1999b), on the basis of low pressures of gas sorption investigations in laboratory find that the sorption capacity measurements would not be influenced by swelling, dissimilar high pressure measurements. Thus, sorption isotherms of CO_2 under low pressures give information relating to the structure of micropores.

Coal is also the natural sorbent characterized by a very heterogeneous structure of organic matter, and with a fraction of micropores that is dominant in relation to the low total porosity (Marecka 2007). The transport mechanism with the small pore sizes is characterised by diffusion. Next, the macropore system is established by the natural fracture network as well as the cleat system. Consequently, this bimodal coal porosity has a large influence on the phenomena, such as sorption capacity (storage capacity) and transport of mine gases (permeability). It has been also shown that the transport in porous coal media depends strongly on the size and nature of sorbate molecules which induce a steric interactions (Marecka 2007).

The mathematical description of a actual processes occurring in complex porous coals is necessary for solution of technical applications, for areas such as storage of gases, environmental protection as well as for modelling of such phenomena. Extensive research on this problem has been developed over the last years. For that reason, knowledge about sorption behaviour of CO_2 and CH_4 is required in the sorption empirical research with simultaneous kinetic studies. The permeability of coal is one of the most critical parameters in estimation of the performance of coal bed and is also the basis for a consideration of the depositing mechanism of carbon dioxide in the coal structure.

In this paper, a comparison of the sorption kinetics process for mine gases (carbon dioxide and methane) in the Polish coals of different rank is presented at ambient temperature and over the pressures range up to 0.1 MPa. The kinetic and diffusional properties of coals are also compared.

Experimental

Under the scheme of experimental studies there have been measured the sorption isotherms and kinetic curves, simultaneously. Were made for two Polish natural coals with the characteristics presented in Table 1 (chemical, technological and petrographic parameters). Selected fractions with 0.5–0.75 mm of coal grains were used for the measurements. The sorbates were CO_2 and CH_4 (Table 2).

The experiments were performed by the classical volumetric method under isothermal-isobaric conditions (at the temperature of 303 K). Prior to measurements, coal samples were degassed at the pressure 10^{-3} Pa. Great attention is given to the experimental difficulties connected with the very slow process of the diffusion of gases in the structure of coals.

The objective of these measurements were the low-pressure single gas isotherms and kinetics of sorption process for coals different ranks from Polish mines.

The factors are discussed affecting the total rate of gas molecules penetration into the microporous coal structure.

Results and discussion

This work is a continuation of a concept discussed in earlier studies. The sorption process may be considered both as static (sorption isotherms) and dynamic denoting the relationship of gas fractional uptake versus time. The sorption process of gases were analysed at equilibrium conditions in our earlier work.

The current study consider the diffusion of mine gases in heterogeneous structure of coal. Experimental kinetic curves of CO_2 and CH_4 sorption are used for comparative analysis. A better understanding of these processes is fundamental for the actual prediction of gas CO_2 injection rates.

However, injection of carbon dioxide and recovery of methane from beds should be considered together.

The porous structure of coal, mostly the microporosity of organic coal matter and the fractures network (with cleats from several microns to microstructures depending on the type of coal) controls the gas transport in a coal beds. And that both processes occur at different rates proportional to the main driving forces. Corresponding to various conditions of coal depth of CO_2 sequestration, coal permeability will varies during gas flow due to changes in the coal structure.

Two Polish coals were selected for this study. As the characteristics of the tested coals in Table 1 show, the samples presents various type of coal with regard to its chemical, proximate and petrographic analysis. They have a quite wide range of Volatile Matter content. The samples differed in vitrinite reflectance (R_o) values (coal 1–2,18%$_{vol}$, coal 2–0,95%$_{vol}$). Next, the both coal samples are dominated by vitrinite group macerals. Inertinite contents range from 14.5% to 16.5%. Coal 1 is characterized by higher content of carbon and lowest content of inertinite group macerals (liptinite is not present) but higher porosity. There is also a good correlation

Table 1. Selected characteristics of the tested coals

Tabela 1. Wybrane właściwości testowanych węgli

Sample	C^{daf} wt %	V^{daf} wt %	A^d wt %	$V_o \cdot 10^2$ $cm^3 \cdot g^{-1}$	Maceral Analysis vol %			
					Vitrinite	Inertinite	Liptinite	Mineral Matter
Coal 1	92.1	8.53	9.10	7.30	83.5	14.5	0	2.0
Coal 2	87.6	27.87	7.78	5.50	83.2	15.8	0.7	0.4

A^d – ash content, C^{daf} – carbon content, , V^{daf} – volatile content, V_o – total pore volume,
Subscripts: ^{a} – analytical state, ^{d} – dry coal basis, ^{daf} – dry ash-free

Table 2. Physico-chemical characteristics of sorbates

Tabela 2. Fizyko-chemiczne właściwości sorbatów

	Molecular weight $g \cdot mol^{-1}$	Critical temperature K	Critical Pressure bar	Critical density $kg \cdot dm^{-3}$	Kinetic diameter nm
Carbon dioxide	44.01	304.46	73.81	0.468	0.330
Methane	16.04	190.55	46.41	0.162	0.380

between value of R_o and carbon content. Hence, the coals were as follows: anthracite sample and medium volatile bituminous rank of coal.

The experimental results of studies are presented in Figure 1. They allow to differentiate between coals. The reason for such behaviour of the kinetic curves are differences in the porous structure of coals under study. The kinetic data revealed a distinct influence of the degree of the coalification on the diffusion rate and on effectiveness of the sorption/desorption process (Clarkson et al. 1999a; Marecka 2007). The uptake of both gases in the microporous structure of coal with the properties of anthracite coal, is much slower in comparison with the diffusion rate in a more available structure of bituminous coal. It is generally accepted that bituminous coals have some orientation whereas anthracite coals are well ordered (crystal like arene domains – van Krevelen 1993). Increasing sorption capacities are attributed to the microporous structure of the coal sorbent. However, diffusion in the microporous coal matrix is very slow, in particular in case of rigid structure of anthracite and especially for CH_4. In consequence of those penetration dissimilarity the carbon dioxide and methane molecules can be also used as the measure of the structural differences of coal sorbents.

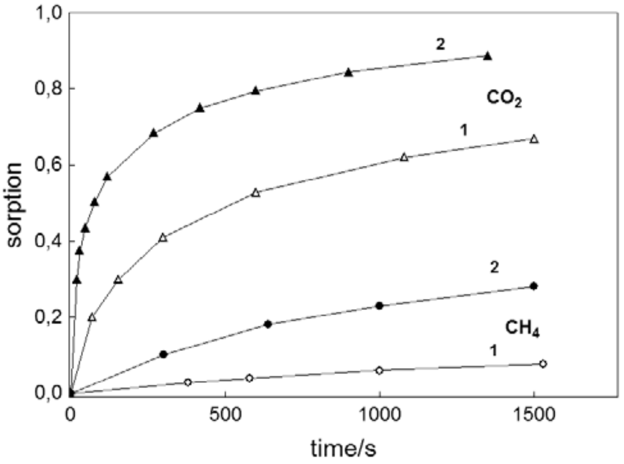

Fig. 1. Kinetic curves for gases sorption on coals (T=303K)

Rys. 1. Krzywe kinetyczne dla sorpcji gazów na węglach (T = 303K)

Further, from this experiments results it is evident that CO_2 sorption rates are always higher by a factor of 2–5 than those for CH_4, when comparing single gas sorption experiments. In addition, CO_2 sorption diffusion rates appears to be higher for all coal ranks and compositions.

When comparing petrographic composition of coals and its effects on gas capacity, it seems that, by increasing the inertinite in bituminous coal there is a decrease in microporosity and an increase in meso- and macroporosity of the coal which reduces the surface area for sorption. Simultaneously, more open porous structure in case of the coal 2 (through the presence of larger pores) will results in faster diffusion with regard to both CO_2 and CH_4 molecules. Microporous coals have higher internal surface area than mesoporous and macroporous coals.

The explanation should take into account also the difference in the physico-chemical properties of gas molecules under experimental condition (ambient temperature) and distance from the critical temperature. Methane molecule is apolar whereas carbon dioxide molecule has quadrupole moment.

One of the most popular model used in sorption studies in coals is the classic approach introduced by Fick. In this model the flux is expressed as being proportional to the gradient of gas concentration causing the transport associated with the Fickian diffusion coefficient. The diffusion coefficient is a macroscopic property, which is related to the gradient of gas concentration as well as the porosity of material in a complicated manner and gas properties. Most analytical methods of the calculation of diffusion coefficients (D, $cm^2 \cdot s^{-1}$) or diffusion parameters (D/r^2, s^{-1}), treated as the fitting parameters, have been defined basing on Fick's II law (for isotropic, homogeneous porous media), using a single parameter diffusion model (Eq. 1) (Cranck 1975):

$$y = -\frac{6}{\pi^2} \cdot \sum_{n=1}^{n=\infty} \frac{e^{-n^2 \pi^2 D \tau / r^2}}{n^2} \qquad (1)$$

where y denotes the fractional uptake, τ is the time (s), D/r^2 represents the diffusion parameter (s^{-1}), and r is the grain radius (cm).

Application of the solution of Eq. (1) to estimate the diffusion coefficient for heterogeneous coal – gas system has become a problem. It is well known, that in coal structure several orders of magnitude of the typical pore size are present together. However, there exist some methods, which at certain approximation enable to simplify the formal difficulties and to estimate diffusion parameters. The most frequently of them is formula for the half-time of the sorption process, while fractional uptake $a/a_{max} = 0.5$ (Timofiejew 1962).

Next, in order to compare diffusion rate of both gases for two coal samples the rate constant k, i.e., the parameter of the kinetic model F2 were also determined. In this semiempirical model the process rate is considered in terms of changes in the fractional uptake versus time, according to the kinetic of second order (Marecka 1998). It should be noted that, in this F2 model the shape of the kinetic curve is taken into consideration. This fact allows to compare the empirical curve over the entire time scale. These both aforementioned models differ in the descriptions of the kinetic data. Finally, in this paper, the kinetic and diffusional properties of coals have been compared (Table 3).

Table 3. Diffusional and kinetic characteristics (T=303K)

Tabela 3. Charakterystyki dyfuzyjne i kinetyczne (T = 303K)

Sample	CO_2		CH_4	
	D/R^2 s^{-1}	k s^{-1}	D/R^2 s^{-1}	k s^{-1}
Coal 1	$0.42\cdot10^{-5}$	$17.24\cdot10^{-5}$	$0.02\cdot10^{-5}$	$2.32\cdot10^{-5}$
Coal 2	$0.36\cdot10^{-3}$	$9.34\cdot10^{-3}$	$0.06\cdot10^{-3}$	$1.59\cdot10^{-3}$

A comparison of the diffusional and kinetic properties of anthracite (coal 1) confirm the observations of the extreme diffusive limitations occurring in the microporous matrix of high rank coal. The fractures have relatively larger permeability than the matrix. For a real application, the diffusion process can be improved by enhancing a number of fractures in coal bed.

To find a more complete analysis the volume pore distribution characteristics of pores larger than 7.5 nm radius (as elemental to the characterization of pore network structure) was determined. A Carbo Erba 1500 mercury porosimeter was used to study these parameters in single experimental run. Pore volume distribution versus a function of their radii data for two tested coals are given in Figure 2. The experimental distribution curves show a somewhat different and complex behaviour. The volume occupied by smallest pores in anthracite coal (in contrast to bituminous coal) increase considerably to a maximum. For bituminous coal this curves remain practically constant in the whole region of the radii values. It can be seen that the PVD curves vary widely in rank and show changes in pore structure of coals which take place in the natural coalification process. For anthracite coal porosity is developed in microporosity. It is well known, that the micro- and submicropores, their presence is connected with the metamorphism and tectonic processes of higher rank of coal. They are coupled with microporosity of coal organic matter. The results of densimetric measurements indicated that the total volume of pores (Table 1) is also higher for the anthracite coal. A relatively lower porosity (and V_o value) of bituminous coal (sample 2) is due to the lowest fraction of finest pores (micropores) in the total volume of pores. The differences in the reflectivity of vitrinite R_o confirm this concept.

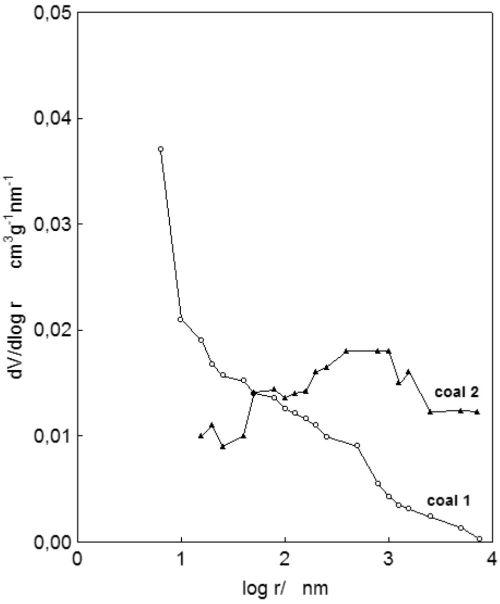

Fig. 2. The graphic presentation of the pore volume distribution

Rys. 2. Graficzna prezentacje rozkładu objętości porów

It should be noted that the observed differences in PVD curves show similar trends with kinetics of gases sorption under study. Moreover, this effect is particularly well visible when the avaibility of the pores is studied by sorptive methods within the range of low pressures. It is evident from the PVD diagrams that distinct differences will be exist in the preferential CO_2 and CH_4 sorption behaviour of two coal samples. A comparison of the diffusional and kinetic parameter values for coal 1 as well as the results of mercury porosimeter investigations (Figure 2) confirm the earlier observation of the extreme diffusive limitations in the pores of this anthracite sample.

This behaviour may be also explained through the low micropore volume of the coal 2 sorbent whereas coal 1 has due to the smaller micropore diameter the higher sorption potential especially at lower pressure which is responsible for its good sorption capacity in this pressure region. Their sorption properties are mainly determined by accessible micropore volume, pore volume distribution and surface chemistry.

Conclusions

This paper summarizes the partial empirical results of mine gases (CO_2 and CH_4) kinetic sorption (in low pressures range and ambient temperature) in two coal samples from Polish mines. For continuous CO_2 injection and exploitation of methane from beds, gas sorption behaviour, diffusion and flow laws must be understood. Injected carbon dioxide can preferentially replace sorbed methane in micropores of coal.

It has been suggested that in the case of conventional reservoir coal beds, the diffusive transport of gas is weak dependent on coal maceral composition and strongly on porous structure and presence of the extreme diffusive limitations occurring in the microporous matrix of high rank coal. No obvious correlations of CO_2 and CH_4 diffusion with rank and composition is observed (Mastalerz 2004). The connectivity of the pore network has a significant effect on the effective diffusion process in porous coals. This fact is essential since this property controls to a major extent the permeability and coal matrix characteristics. In the other hand, the main deciding factors for successful recovery of methane from beds are desorption rate (inversely proportional to the diffusion coefficient for sorption process) and permeability of the beds.

Further research is needed for identify a mechanism of CO_2 diffusion in the coal sorbent.

Acknowledgements

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Kinetyka sorpcji metanu i dwutlenku węgla na węglach polskich

Podjęto badania eksperymentalne kinetyki sorpcji metanu i dwutlenku węgla z powodu problemów przechwytywania i magazynowania gazu. Zastosowano klasyczną metodę wolumetryczną w warunkach izotermiczno-izobarycznych.

Głównym celem badań było wykazanie wpływu stopnia (skład chemiczny i petrograficzny) i co za tym idzie również struktury porowatej na właściwości kinetyczne węgli. Wyniki dla różnych rodzajów węgla z polskich kopalń zostały poddane porównaniu.

Badania związane z kinetyką sorpcji mogą dostarczyć dane pomocne w przewidzeniu wydajności magazynowania gazu (sorpcji) w złożach węgla. Temat ten stał się szczególnie interesujący w ostatnich latach ze względu na ideę sekwestracji CO_2 *w podziemnych formacjach geologicznych (technologia ECBM), w złożach węgla niezdatnego do wydobycia.*

Słowa kluczowe: węgiel, kinetyka sorpcji, sekwestracja CO_2