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## **Sorption and diffusion investigations of gases on coals in the aspect of carbon dioxide sequestration and methane recovery**

### Key words

Coal porosity, sorption, diffusion, carbon dioxide, methane

### Abstract

In the recent years, there can be observed an interest in the problems of CO<sub>2</sub> sequestration. The idea is for coalbed methane, produced following the injection of the CO<sub>2</sub> into deep coal seams. This problem is closely connected with the sorption investigations of the system: coal – CO<sub>2</sub>/CH<sub>4</sub>, the results of which may supply information essential for better recognition of the behaviour of gases in these processes. They are the bases for the description and modelling of processes in situ.

In this work, the influence of the rank and hence also of the porous structure on the sorption properties and diffusion was studied by means of CO<sub>2</sub> and CH<sub>4</sub> sorption in two Polish coals.

### Introduction

The development of industrial production causes permanent increase of gas pollution of the atmosphere as a result of the combustion of solid, liquid and gaseous fuels. This development is closely connected with the increasing demand for energy such as electricity and heat in the XXI century. Moreover, one can observe also increased interest in the problems of pure technology of coal use (Clean Coal Technology). They offer one most effective use of energy from coal and simultaneously the possibility of solving the problem of limiting the greenhouse gas emissions. At the same time, there must be noticed the tendency

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in the world to reduce CO<sub>2</sub> emission by means of more effective use of the primary energy carriers, fast development of the renewable energy sources and introduction of payments for excessive emission (Jestin 2007; Mokrzycki 2004).

The increased recognition and people awareness of the global warming issue have resulted in an international legislation the Kyoto Protocol in 2005. Carbon dioxide is dominant greenhouse gas. Measured atmospheric CO<sub>2</sub> concentrations for the last two hundred years show that the concentration of this gas has increased from 270 to 370 parts per million in atmosphere. There are many mechanisms responsible for the warming of about 0.4–0.6 K observed for the last century.

One possible solution to reduce anthropogenic CO<sub>2</sub> is geologic sequestration of carbon dioxide, including deep saline aquifers, oil and gas reservoirs and unmineable coal seams. A review of various technologies connected with these problems can be found in the widely presented literature (among others, in the studies by Bachu 2002; Jestin 2007; Marzec 2001; Tarkowski 2003).

Methane is present practically in all coal seams as a gas deposited in its structure. Further, there can be observed increased interest in methane as ecological source of energy and its recovery from the coal seams in recent years.

Sorption experiments can be used to study different characteristics of coal properties, among other things, gas content, gas diffusion, porosity. Basing of the present state of knowledge of the coals structure, especially of their porous structure, recognized thanks to the sorption investigations, there has been presented the interpretation of the obtained results of the measurements in the aspect of the problems of CO<sub>2</sub> storing in unmineable coal seams to recover the methane. These investigations contribute to better understanding of the interaction of gases with coal surface and diffusion in coal.

### **1. Storing of CO<sub>2</sub> in coal beds**

The concept of using microporous solid bodies as gas collectors, competitive in comparison with other unconventional methods of storing the gases has been known for many years.

It is well known that carbons and zeolites can possess molecular sieving properties due to their specific porous texture. Hence, they have been widely used for purification and separation in various areas, together in ecological aspect.

On the other hand, coal is natural raw material whose better utilization in the processes of environmental protection and counteracting the negative results of excessive gases emission, in the last decade became connected with the development of the sorption technology of CO<sub>2</sub> storage (CCS – Carbon Capture and Sequestration) in the geological underground structures. In general, these technologies are connected with capturing CO<sub>2</sub> directly from its source and its storage at a safe depth. The process of gas deposition in coal beds should be carried out under conditions quaranteeing long-term stability of the reservoir system, best for geological time scale.

Not all the mentioned problems are at present sufficiently recognized, especially in the aspect of the permeability of the coal beds. The problems of mass transport and sorption/desorption of CH<sub>4</sub> and CO<sub>2</sub> on/from coal surface are also connected with such phenomena as the emission of gas from the seams or sudden rock and gas outbursts. Depending on the condition these processes may proceed at various rates.

The geological conditions (the problem of selecting the coal seam) are of great importance in the adsorption technology of CO<sub>2</sub> storing. This mechanism is that the dioxide carbon displaces the sorbed methane and the injected CO<sub>2</sub> is sequestered in the reservoir by sorption on the coal surface (ECBM – Enhanced Coalbed Methane). The sorption investigations contribute to the understanding of both storage and recovery processes. It is important to note that their results can be viewed mainly as a convenient basis for comparative studies of different type of coals and mine gases.

## 2. Coal porosity

Coal porosity is the volume fraction of coal, which may be occupied by gas molecules. The measurement of coal porosity with different gases/vapour is a very complex problem and both the size of gas molecules and their relation to the coal structure have to be taken into consideration. Coal also contains inherent moisture in the seam in the natural state.

In fact, coal seam is characterized by a dual porosity which consists of micropore and macropore systems. The microporosity is contained in the coal matrix (highly heterogeneous). The majority of coalbed methane is present in the sorbed state in these micropores, particularly at low pressure range. Next, the macropore system is established by the natural fracture network as well as the cleat system. Heterogeneity of coals can be also discussed in connection with the presence of various group of macerals (Karacan 2003). Moreover, the nature of the porosity of coals changes in a characteristic way in the coalification process (Marecka 2001, 2007).

Consequently, this bimodal coal porosity has a large influence on the phenomena, such as sorption capacity and transport of gases.

In the mining practice considerable changes in the permeability of the bed have been also observed as a result of such phenomena as swelling and shrinkage of coal during the sorption and desorption processes depending on the pressure of gases.

## 3. Experimental

Investigations have been conducted for the sorption of CO<sub>2</sub> and CH<sub>4</sub> on two Polish coals of various rank (from medium to low content of volatile parts) and porosity.

Measurements were performed by the volumetric method (isothermal-isobaric conditions), for low pressures (up to 0.1 MPa) and ambient temperature (303 K), on a coal samples with the same coal grain size (0.49–0.75 mm).

Selected characteristics of tested coal as well as physico-chemical properties of the used sorbates are given in Tables 1 and 2.

TABLE 1

Selected results of chemical and technological analysis of examined coals

TABELA 1

Wybrane rezultaty analizy chemicznej i technologicznej badanych węgla

Sample	C <sub>daf</sub>	V <sub>daf</sub>	A <sup>d</sup>	M <sup>a</sup>	V <sub>(mic+mes)</sub> *	ρ <sub>He</sub>	Type of coal
	wt %	wt %	wt %	wt %	cm <sup>3</sup> ·g <sup>-1</sup>	g·cm <sup>-3</sup>	
Coal 1	92.1	8.53	9.10	0.78	0.064	1.46	42.0
Coal 2	87.6	25.38	7.78	1.25	0.024	1.40	37.1

\* Micropore and mesopore volume determined from total pore volume and the measurements of mercury porosimetry.

TABLE 2

Important physico-chemical characteristics of sorbates

TABELA 2

Ważniejsze fizykochemiczne charakterystyki sorbatów

	Molecular weight	Critical temperature	Critical density	Kinetic diameter
	g·mol <sup>-1</sup>	K	g·cm <sup>-3</sup>	nm
Carbon	44.01	304.46	0.468	0.399
Methane	16.04	190.55	0.162	0.388

#### 4. Results of sorption experiments

The sorption investigations in the system: coal – gases require appropriate preparation in laboratory and, first of all, the proper interpretation of the results. Great attention is given to the experimental difficulties connected with the very slow process of the diffusion of gases in the structure of the coals, determined by the needed for the establishment of sorption equilibrium. On the other hand, the advantages of low pressure kinetics investigations of the sorption process (up to 0.1 MPa) are manifested in the possibility of characterizing coal in the aspect of its natural properties, i.e. in the estimation of the availability of the coal structure for the molecules of the sorbed gases. As it is well known, the decisive role is that of the microporous structure of coals (connected with the coal matrix) and the nature of the gas molecules (Marecka 1995).

As mentioned above, sorption experiments contribute to extend knowledge about the accumulation and behaviour of mine gases within the coal bed. In the present study, results

of the sorption and diffusion of  $\text{CO}_2$  and  $\text{CH}_4$  on selected two Polish coals with respect to their porous structure, are presented.

Figure 1 illustrates (by way of example) the isotherms of  $\text{CO}_2$  sorption on the tested coals. From Figure 1, it is evident that the sorption capacities increase systematically with increasing rank coals. In turn, results of the  $\text{CO}_2$  and  $\text{CH}_4$  measurements (of mine gases) clearly shows the distinct difference in the sorption uptake with respect to both gases. Literature data and this work indicate that the sorption of methane is generally about two times lower than that of coal dioxide on Polish coals. Carbon dioxide, because of its kinetic diameter and physico-chemical properties (characterized by a critical temperature and a quadrupole moment), has a better access to micropores. Hence, all the sorption results obtained on the same grain size of coal samples, allowed to trace the changes in the porous structure in coals of various degree of metamorphism. The structure of coal pores (a rock medium) has a decisive influence on the specific physico-chemical properties, such as e.g. sorption or storing capacity as well as ease of permeability of the coal bed. All the investigation results of this study and literature data have confirmed that the degree of the development of the microporous structure (Table 1) determines effectiveness of the sorption/desorption process (Marecka 1995; Clarkson 1999) and as a consequence the storage of carbon dioxide and recovery of methane.

Kinetics sorption measurements are also of great importance in the adsorption technology of  $\text{CO}_2$  storage. For instance, gas diffusion experiments at low pressures, as in this study, may indicate the role of the finest pores in accumulation and recovery processes. Moreover, this investigations may provide complementary analysis for the description and modelling of processes in situ.

The experimental and theoretical factors determined the possibility of analysis of the sorption kinetics data.

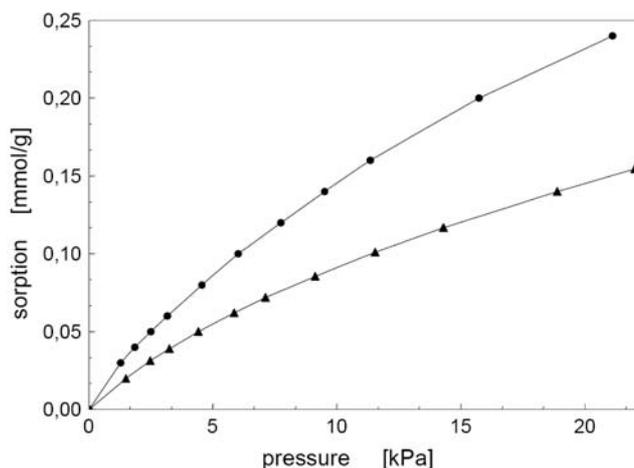


Fig. 1. Isotherms of  $\text{CO}_2$  sorption on examined coals

● – coal 1; ▲ – coal 2

Rys. 1. Izotermy sorpcji  $\text{CO}_2$  na badanych węglach

● – węgiel 1; ▲ – węgiel 2

The empirical factors are connected with the real properties of natural coal sorbents. The kinetics of sorption process of carbon dioxide and methane in coals have been presented by means of the solutions of Fick's II law using a single parameter diffusion model. The values of the diffusion parameter, which is fundamental property of a coal – gas system, were calculated on the basis of an analytical solution of a differential equation:

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

where:

- $y$  — fractional uptake,
- $\tau$  — time, s,
- $D/r^2$  — diffusion parameter,  $s^{-1}$ ,
- $r$  — grain radius, cm.

The diffusion rates of CO<sub>2</sub> and CH<sub>4</sub> in examined coals were greatly different. The differences in the diffusion parameters  $D/r^2$  between the coals (Table 3) may be also associated with changes of the development of the internal surface of coal and with the different fraction of micropores in the total volume of pores during the coalification process. Thus, coal 1 (anthracite), with higher ordering of its structure, is characterized by a very slow sorption and desorption of CH<sub>4</sub> (in spite of its relatively high sorption capacity). In addition, the petrographic analysis, has confirmed that this coal is composed of vitrinite and macerals of inertinite group. Carbon dioxide diffuses faster into the microporous structure. The obtained kinetics data have confirmed the earlier suggestion that the sorption phenomena and accumulation of gases in coal, through the mechanism of physical sorption, is primarily determined by the presence of micropores, a considerable part of which comprise pores of sizes comparable with the dimensions of the diffusing gas molecules (<0.5 nm), and the access to which is rather difficult (Marecka 1995).

Depending on the actual conditions of pressure and temperature and the type of coal the processes of the release of the mine gases (among other, CO<sub>2</sub> and CH<sub>4</sub>) will proceed at

TABLE 3

Diffusion parameters for sorption CO<sub>2</sub> and CH<sub>4</sub> on examined coals (determined from Fick's II law)

TABELA 3

Parametry dyfuzji dla sorpcji CO<sub>2</sub> i CH<sub>4</sub> na badanych węglach (wyznaczone na podstawie II prawa Ficka)

	D/r <sup>2</sup> , s <sup>-1</sup>	
	coal 1	coal 2
CO <sub>2</sub>	0.42 · 10 <sup>-5</sup>	0.36 · 10 <sup>-3</sup>
CH <sub>4</sub>	0.02 · 10 <sup>-5</sup>	0.06 · 10 <sup>-3</sup>

various rate. It should be stressed here that carbon dioxide considerably easier penetrates the structure of the micropores of a coal matrix in comparison with methane (Marecka 1995). When however considering the transport phenomena in a coal seam attention should be given to the non-uniform bimodal character of this phenomenon comprising the flow of gas (pore fluids) under the influence of the pressure gradient (convection) in large pores and fissures as well as the diffusion processes in the narrow pores of a coal matrix determined by the gradient of concentration of gases (Marecka 2005). It is assumed that the transport of gases in coal could be analysed at this two scales. However, this complicates presentation of the transport phenomena will determine the total permeability of the coal bed (Marecka 2007).

Theoretical factors results directly from the consideration of the mathematical description of the empirical kinetics data. The problem becomes crucial in modeling of this process based on classical diffusion model. It is obvious that the because of the complexity of the sorption diffusion phenomena in coal matrix any theoretical description of these processes will be merely a rough approximation. For such purpose, suitable coal – gas system should be selected for which all necessary simplifications are acceptable. In this context, in the present study, the sorption measurements were carried out on more modelled coal sorbent, i.e. anthracite (coal 1 in Table 1), demonstrating a considerably higher degree of structure ordering. Moreover, before estimating the diffusion coefficients there must be carried out the analysis of the correctness of the kinetics curve shape obtained experimentally and calculated on the basis of the classical diffusion model, e.g. from Fick's II law. These theoretical studies are continued. This problem is connected with the search for the most accurate kinetic characteristics of the systems: coal – CO<sub>2</sub>/CH<sub>4</sub>.

Reasuming the literature data and the results of the present study it can be demonstrated that the geological conditions (the problem of selection coal seam in aspect of the its permeability) are of great importance in the adsorption technology of CO<sub>2</sub> storage.

## Conclusions

In recent years, the capture and the underground storage of carbon dioxide have been considered as an option for reducing greenhouse gas emissions.

CO<sub>2</sub> storage and transport properties of two coals from Polish mines were measured depending on coal rank. The measurement results show that the CO<sub>2</sub> storage capacity is about twice that of CH<sub>4</sub>. The diffusion parameters (estimated from experimental curves basing on Fick's II law) of CH<sub>4</sub> in coal structure are significantly lower that the CO<sub>2</sub>. Important problem is the selection of the method of mathematical description of the experimental kinetic data.

The application aspect of ECBM technology is connected with the displacement of methane present in the coal bed by an easier sorbed gas, i.e. CO<sub>2</sub> and the selective transport of both gases in the coal matrix. The essential problem in these processes are the sorption

interactions of carbon dioxide with the storage medium, which are mainly determined by the degree of the metamorphism (type of coal) and hence also by the structure of coals.

As it has been shown in the investigations (Marecka 1995, 2005, 2007) the problem are the coal beds of low permeability determined by their particularly complex geological structure.

Anticipation of CO<sub>2</sub> behaviour in coal seam and the characteristics of the processes of mass transport requires also the knowledge of coal porosity in the bed. There must be taken into consideration the effect their porosity on transport phenomena as well as the geo-mechanical conditions of the coal bed and the neighbouring rocky layers.

Analysis of the literature data indicated that the main barrier in the designing and modelling of the process of underground CO<sub>2</sub> storage, e.g. unmineable coal is the high cost (Jestin 2007).

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**SORPCJA I DYFUZJA GAZÓW W WĘGLACH KAMIENNYCH W ASPEKcie SEKWESTRACJI DITLENKU WĘGLA  
I POZYSKIWANIA METANU**

**Słowa kluczowe**

Porowatość węgla, sorpcja, dyfuzja, ditlenek węgla, metan

**Streszczenie**

W ostatnich latach obserwuje się zainteresowanie problematyką sekwestracji CO<sub>2</sub>. Koncepcja podziemnego składowania CO<sub>2</sub> w głębokich pokładach węgla kamiennego rozważana jest równocześnie z pozyskiwaniem metanu.

Problematyka ta pozostaje w ścisłym związku z badaniami sorpcyjnymi w układzie: węgiel kamienny – CO<sub>2</sub>/CH<sub>4</sub>, których wyniki mogą dostarczyć informacji istotnych dla pełniejszego poznania zachowania się gazów w tych procesach. Badania te stanowią podstawę do opisu i modelowania procesów zachodzących *in situ*.

W pracy przedstawiono wpływ stopnia metamorfizmu, a stąd także struktury porowatej węgla na właściwości sorpcyjne i dyfuzję CO<sub>2</sub> i CH<sub>4</sub> na dwóch węglach kamiennych z polskich kopalń.