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Interactions between CH_4 and CO_2 gas mixtures and hard coal in the context of potential sequestration of carbon dioxide in underground sites in Poland

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Abstract

The purpose of this study is to find the relationship between the low-pressure sorption of the gas mixture CO_2 and CH_4 and properties of coal in the context of geological conditions in the coalbed. These aspects give us a better insight into the interactions between gas mixtures and coal, enabling us to forecast the long-term effects of CO_2 storage. In the light of the length of the process and stability of such systems, it is required that physical properties of coal be identified first. A great deal of information can be obtained from sorption isotherms, relating to physico-chemical properties of the sorbent. Test results reveal the relationship between the coal rank and vitrinite reflectance and the sorption capacity of investigated coals.

Keywords: sequestration, sorption, gas mixture, coal

Introduction

Extensive experiments on sorption/ desorption of gases under elevated/reduced pressures have clarified the mechanisms of interactions between mine gases and organic matter contained in coal. It is required that physico-chemical properties of coal should be known and experimental tests are of key importance for control of the state of stress in the rock strata in the context of rock and gas outburst prevention and CO_2 sequestration in water-bearing features [Kelemen and Kwiatek, 2009; Baran et al., 2010; Garnier et. al., 2011]. The safety of sequestration projects is associated with sorption/desorption of mine gases, particularly CH_4 and CO_2 and changes in coal's porosity induced by these processes, variations in its permeability and the risk of methane explosion in coalbeds. Differences in coal's behaviour with respect to gases are attributable to different physico-chemical properties of CO_2 and CH_4 and heterogeneity of coal being the consequence of the coalbed's structure and geological history. The course of the sorption process depends to a large extent on the coal's structure and its capillary features, and hence its sorption capacity. Porosity is closely related to the degree of metamorphism and its petrography. With the higher coal rank, the contents of molecular pores increases, this feature is well demonstrated by vitrinite. Results of sorption tests using various sorbates and carried out under variable conditions suggest that hard coal have the best developed system of micropores [Rodrigues and de Sousa, 2002; Busch et al., 2003; Gruszkiewicz et al., 2009]. The micropore size is comparable to that of molecules of adsorbed/absorbed substances. Therefore, the contribution of macropores and mezopores to the sorption capacity of coals is of minor importance yet they play a major role in the gas migration and transport processes. Hard coals are considered to be heterogeneous sorbents, also referred to as biporous systems. Retention of coalbed gases involves adsorption on the surface, absorption in the coal's molecular structure in the form of free gas in pores and as a substance dissolved in ground waters contained in the coalbed.

Sorption of single low-molecule substances on hard coals has received a great deal of attention in the context of physico-chemistry of coals. However, the complex physico-chemical nature of those sorbates further complicates the interpretation and forecasting of their sorption capacity respective to those substances. Literature on the subject still lacks a clearly established relationship between the sorption of a gas on coal and its physical and chemical properties, associated with coal rank and type [Mastalerz et al., 2004; Yu et al., 2008]. On account of the presence of gas mixtures in coal, particularly the mixture of CH_4 and other gases which entail the risk of a gas and rock outburst, tests of CO_2 and CH_4 sorption seem fully justified and merited in the context of burst control measures and potential sequestration of CO_2 in coal.

Methodology

Hard coal samples from collieries in the southern and western Poland were collected in accordance with the procedure set forth in the standard PN-90/G-04502.

The results of the elemental analysis of investigated coal samples are summarised in Table 1. The technical and petrographic data are compiled in Table 2.

Table 1. Characteristics of the coal samples investigated

Coal	*A* [%]	V^{daf} [%]	C^{daf} [%]	Porosity f_V [%]	Real density d_{He} [g/cm^3]
B	2.77	33.40	84.14	15.07	1.45
RM	4.96	22.32	90.12	4.50	1.34
P	3.01	27.12	84.24	3.24	1.26
M	2.86	30.40	79.46	4.32	1.33
C	2.65	35.62	79.29	7.45	1.27
Z	8.92	27.93	78.62	3.48	1.10
SM	14.18	29.88	70.82	3.38	1.27
J	14.45	28.39	57.83	15.86	1.37

Table 2. Petrographic analysis of studied coal

Coal	Group of macerals [%]				
	Vitrinite	Liptinite	Inertinite	Mineral substance	Reflectivity
B	46.6	12.5	32.4	5.7	0.74
RM	63.7	3.3	32.7	0.8	1.18
P	73	7	20	1	0.92
M	38	9	53	2	0.72
C	60	10	30	1	0.70
Z	91	1	8	4	1.01
SM	60	9	31	14	0.78
J	67	5	28	11	0.51

Sorption tests use coals with the vitrinite content ranging from 38-91%. The largest proportion of vitrinite is registered for coal from the colliery *Z*, the lowest-from the colliery *M*. The maceral contents of the egzinite group ranges from 1.0-12.5%, inetrinite: 8.0-53.0. Sorption capacity tests reveal that the vitrinite reflectance of the investigated coals ranges from 0.70 to 1.18%. the highest value of this parameter is registered for coal from the colliery *RM* and the lowest-for that from the colliery *C*. Testing done at the AGH-UST by the mercury porosimetry and helium density measurement methods reveals the coal porosity to be in the range 3.24-15.86%. The coal from the colliery J has the highest porosity, which may suggest, at this stage, its specific sorption capacity with respect to CO_2, on the surface and in the coal bulk. Coal samples with the lowest pore contents are those from the collieries *SM* and *P*.

Measurements of sorption of gas mixtures containing 50% CO_2 and 50% CH_4 on hard coal samples were taken in the laboratory scale using the sorption meter ASAP 2010 (Micrometrics) intended for volumetric measurements. Colas were first ground to average their physico-chemical parameters, in accordance with the procedure set forth in the technical standard PN-90/G/04529. Before the tests began, thus prepared coal samples, with the grain size 0.5-0.7 mm, were kept in the nitrogen atmosphere. Prior to the measurements, the samples were evacuated under vacuum, at 10^{-3} Pa.

Results and discussion

Sorption isotherms (Fig. 1) reveal that the lowest rank coal *J* has the highest sorption capacity, while coals from the collieries *SM* and *RM* have the lowest sorption capacity. These coals have low porosity and the coal *RM* is a high rank coal, and its vitrinite reflectance is the highest. As the applied sorbate had an identical composition, this fact should be attributable to differences in the (degree of metamorphism) coal rank and petrography.

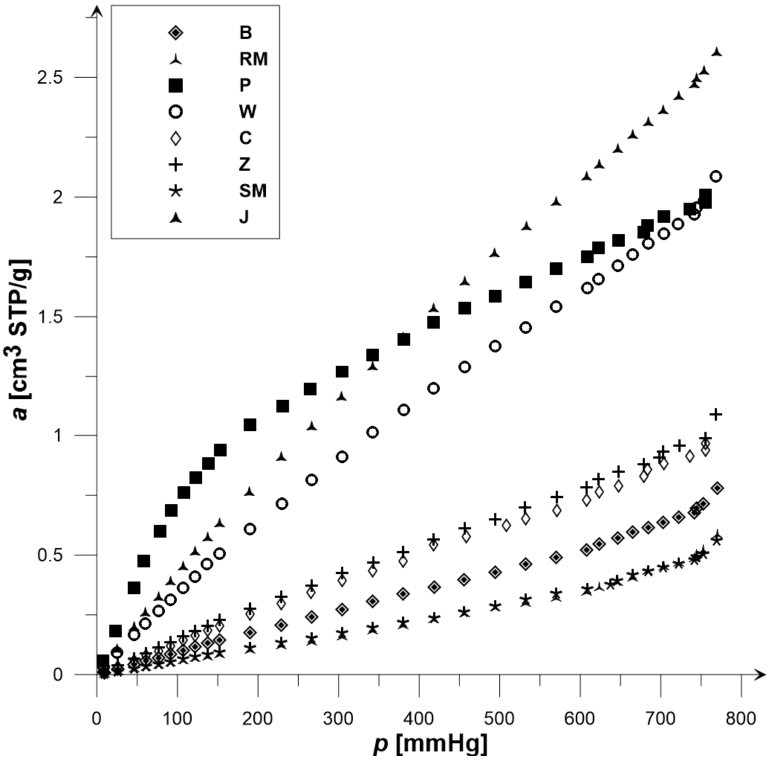

Fig. 1. Isotherms of low pressure mixture of CH_4+ CO_2 sorption

The coal *J* has the highest porosity and its vitrinite reflectance is the lowest. Coals *SM* and *RM* have a low porosity and the coal *RM* is a high rank coal and its vitrinite reflectance is the highest. It is found out that although the micropore volume tends to increase with the coal rank, the sorption capacity of investigated coals decreases with the carbon (C) contents. No relationship is found between the sorption capacity and maceral (organic matter) content (Fig. 2-4).

Results shown in the form of graphs suggest that the coal rank is a major determinant of the sorption capacity of coals respective to methane. Coal with a lower carbon (C) content has a number of low-molecular bonds (it is a mobile phase) and the present macromolecules of a coal copolymer display a low degree of ordering, hence the coal structure is sufficiently loose and all molecules of the gas mixture being separated tend to diffuse to the pore interior wherein the sorption process takes place. Separation of the two gases is possible due to the difference in the value of the sorption equilibrium (the separation mechanism involving the equilibrium effect). Coals with the higher level of metamorphism have a small number of low-molecular bonds and a great number of well-ordered molecules. Hence their structure is more rigid than in low rank coals and not so easily penetrable by gas and vapour molecules as pores are less accessible. The gas mixture can be separated thanks to the differences in the diffusion rates of molecules through pore narrowing, where smaller molecules tend to get sorbed faster than larger ones (the separation mechanism involving the kinetic effect). Restricting ultramicropores make the coal behave like a molecular sieve activating the gas diffusion mechanisms. This model of the pore structure restricted by ultramicropores fully explains why the dimensions of coal molecules determine the gas uptake and the process of reaching the sorption equilibrium. As the molecule dimensions decrease, numerous restricted pore openings widen whilst other pores, insofar closed, become accessible to molecules of the adsorbate. The molecular dimensions of the sorbate and porous structure of the sorbent strongly influence the selective sorption and diffusion processes

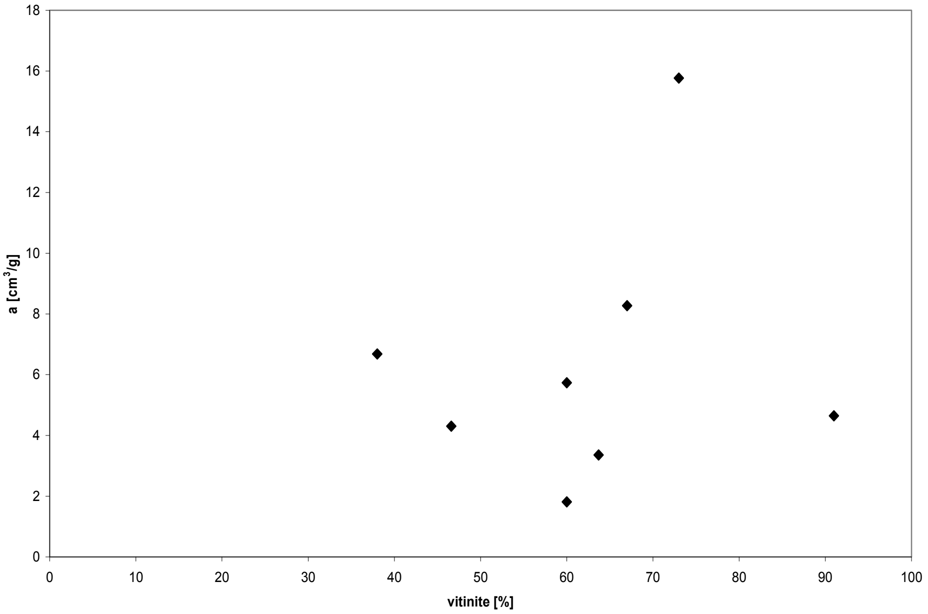

Fig. 2. Dependence of sorption capacity from vitrinite content

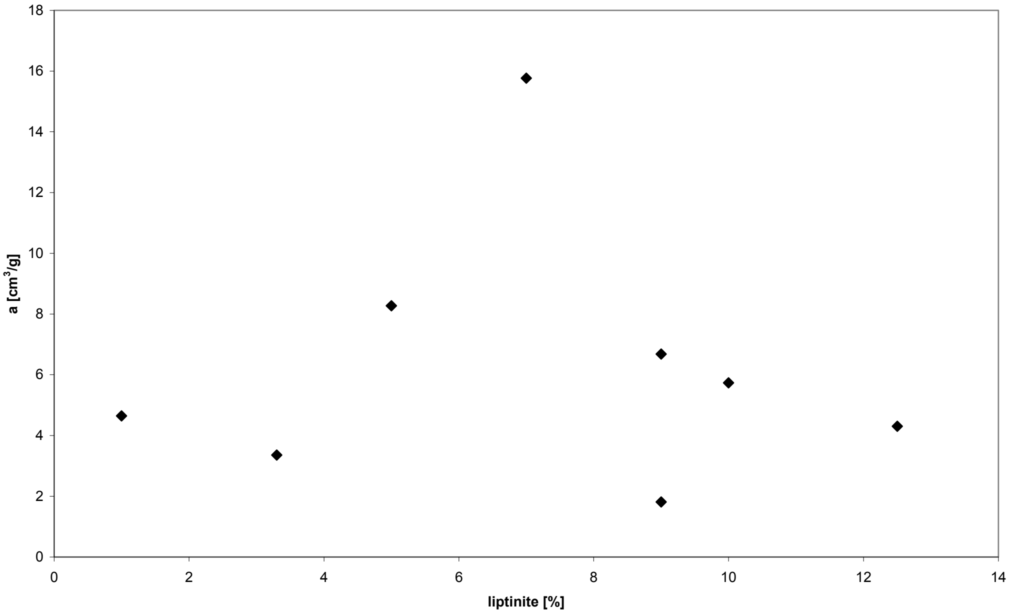

Fig. 3. Dependence of sorption capacity from liptinite content

[Cui et al., 2004; Zarębska and Ceglarska-Stefańska, 2008; Pan and Connell, 2012]. The selective behaviour in this case is the consequence of energy (adsorption affinity) and the kinetic diameter of gas molecules. The favoured process is that of sorption of molecules exhibiting higher adsorption energy and the lowest kinetic diameter. Carbon dioxide satisfies these two requirements as it displays smaller kinetic diameter and higher kinetic energy than methane and hence it is able to diffuse to the macroporous matrix much more easily than methane. Besides, the coal matrix is able to absorb a larger amount of carbon dioxide than of methane. Better affinity of carbon dioxide to a porous structure is due to its physico-chemical as well as electric properties (the quadrupole moment) and to the presence of functional groups in hard coal. Reactive oxygen groups present in the structure of the coal copolymer restrict the access of CH_4 molecules to pores, while in the case of CO_2 the interactions with those oxygen groups appear to be very specific [Clarkson and Bustin, 2000; Ceglarska-Stefańska and Zarębska, 2001]. The coal copolymer contains a heterogeneous network of interconnected pores, narrowed down to the ultramicropore size, it appears that this structure should be easily penetrable to CO_2 with the kinetic diemeter 0.33 nm instead of CH_4 whose kinetic diameter equals 0.38 nm. The selective sorption of CO_2 is also caused by differences in the boiling temperatures

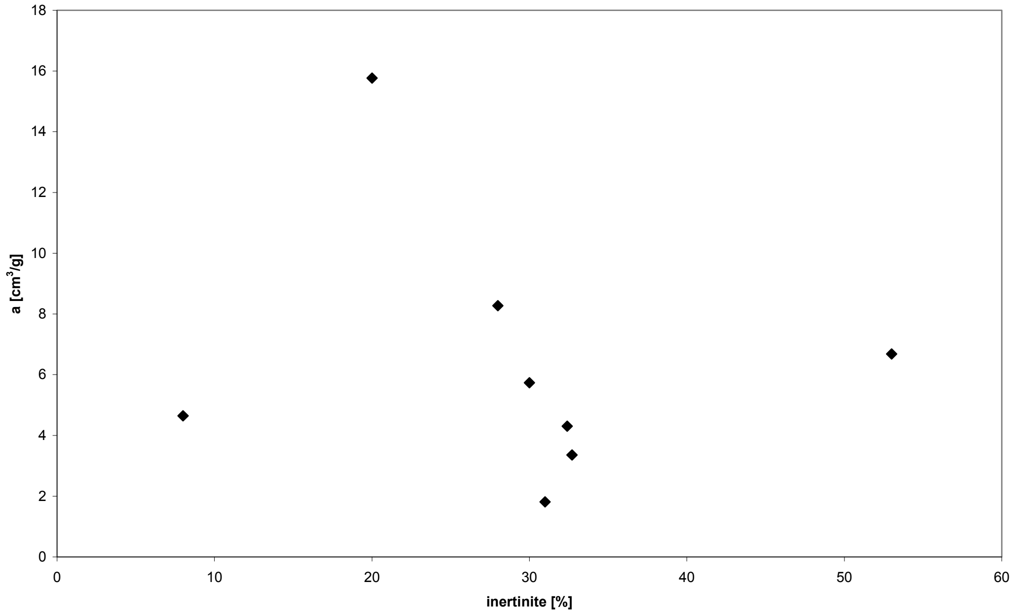

Fig. 4. Dependence of sorption capacity from inertinite content

between CO_2 and CH_4. The boiling temperature of carbon dioxide is higher (194.5 K) whilst for methane it is 114.4 K. That is why sorption affinity for this gas is better than for methane [Mastalerz et al., 2004; Dutka et al., 2013; Wierzbicki, 2013]. In an attempt to answer the question why the sorption value for CO_2 is higher than for CH_4, Mastalerz and others [2004] found out that the reason is the tendency of CO_2 to be adsorbed not only in micropores, but also in mezopores by way of multiple layer sorption. Differences in the sorption mechanism are also attributable to the fact that in the case of methane the gas is adsorbed in micropores whilst CO_2 gets adsorbed in micropores and absorbed in the elastic organic structure [Majewska and Ziętek, 2007; Skoczylas, 2016; Wierzbicki, 2017].

Conclusions

The results of sorption tests carried out in the low-pressure range of the sorbate substance suggest that in the systems comprising hard coal and gas mixture of CO_2 and CH_4, the favoured process involves the adsorption of CO_2 molecules in the structure of the coal. Comparison of isotherms reveals that differences in physico-chemical structure of coals, associated with the coal rank, determine the sorption capacity of coal obtained under similar conditions. It is reasonable to suppose that these factors should be treated as determinants governing the state of stress in the coalbeds and thus produced strains can cause the changes of the gas pressure and permeability.

Sorption tests using gas mixtures do not reveal any relationship between the content of particular macerals and the value of sorption capacity. A relationship is found between sorption capacity and the coal rank of investigated sorbents. The maximal sorption capacity respective to the gas mixture CO_2 and CH_4 is registered for the lowest-rank coal whose vitrinite reflectance is the lowest, too. No relationship is found between sorption capacity and the petrography of investigated samples.

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Analiza oddziaływań mieszaniny gazów CH_4 i CO_2 z węglem kamiennym w aspekcie możliwości podziemnego składowania ditlenku węgla w regionie Polski

Streszczenie

Celem pracy było znalezienie powiązań między przebiegiem procesu niskociśnieniowej sorpcji mieszaniny gazów CO_2 i CH_4, a właściwościami węgla kamiennego, w odniesieniu do konkretnych warunków geologiczno złożowych. Informacje te są istotne zarówno ze względu na możliwość uzyskania danych dotyczących oddziaływania mieszaniny gazów z węglem, jak również prognozowanie ewentualnych skutków długoterminowego składowania CO_2. Uwzględniając długotrwałość procesu oraz stabilność takiego układu niezbędne jest dokładne poznanie fizycznych właściwości węgli. W tym celu pożądanych istotnych informacji dostarczają izotermy sorpcji, w połączeniu z właściwościami fizykochemicznymi sorbentu. Analiza uzyskanych wyników pozwoliła na wykazanie zależności wpływu stopnia uwęglenia i współczynnika odbicia światła witrynitu na wartość chłonności sorpcyjnej badanych węgli.

Słowa kluczowe: sekwestracja, sorpcja, mieszanina gazów, węgiel