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ON THE EFFECTS OF MACERAL CONTENT ON METHANE SORPTION CAPACITY IN COALS

WPLYW ZAWARTOŚCI MACERAŁÓW NA POJEMNOŚĆ SORPCYJNĄ METANU W WĘGLACH

The problems connected with the sorption capacity of methane in hard coals are constantly subject to various research. In this paper, the influence of the content of macerals mainly vitrinite for the sorption capacity of chosen samples of Polish hard coals was analysed. The analysis was conducted on basis of available from the literature results of resarches of petrographic composition of this coals and methane sorption isotherms. The samples of grained coals contained from 7 to 76% of vitrinite and their sorption capacity was obtained in the scope of high pressures; $0 < p < 80$ bars, on the basis of the equation of Langmuire. In effect, it turned out that the maceral content has a little influence on the methane sorption capacity of coals. This refers mainly to high volatile and middle volatile coals. In the literature concerning this issue simillar effect may be encountered for other coals.

Keywords: methane sorption capacity, macerals, vitrinite, inertinite

Problemy związane z pojemnością sorpcyjną metanu w węglach kamiennych są nadal przedmiotem różnych badań. W tym artykule przedstawiono wpływ zawartości macerałów, głównie wityrinitu na pojemność sorpcyjną wybranych prób polskich węgli. Przeprowadzone analizy były oparte o wyniki badań dostępnych w literaturze odnośnie do składu petrograficznego tych węgli oraz ich izoterm sorpcji metanu. Dotyczy to próbek ziarnistego węgla, w którym zawartość wityrinitu wynosiła 7-76%, a ich pojemność sorpcyjna była wyznaczona w zakresie ciśnienia 0-80 bar, w oparciu o równanie Langmuira. W efekcie tej pracy okazało się, że zawartość macerałów w węglu ma mały wpływ na pojemność sorpcyjną metanu w tych węglach. Dotyczy to głównie węgli o wysokiej i średniej zawartości części lotnych. W literaturze można spotkać podobny do tego efekt, dotyczący innych rodzajów węgli.

Słowa kluczowe: pojemność sorpcyjna metanu, macerały, wityrinit, inertynit

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1. Introduction

Methane in coal bed (CBM) occurs mostly in absorbed gas on pore surfaces and in volume absorbed in coal matrix (dissolved gas). Methane is also present in small quantities in free gas in the fracture network. The characterization of CBM reservoir is complex due to the high degree of heterogeneity and variation in maceral composition of coal. However, the influence of petrographic composition of Polish coal on the methane sorption capacity is not well understood. Besides that, coal rank influences the methane sorption capacity and may mask the effects of the maceral composition. The relationship between on the one side the coal type, i.e. maceral composition and coal rank and on the other the methane sorption capacity is also not fully understood. Coal rank may be determined by a variety of physical and chemical properties, which are connected with the coal type. Vitrinite and inertinite are main components of coal.

Generally the internal surface are progressively increases with declining pore size in a coal structure; the reason why vitrinite can store more methane than inertinite is because vitrinite is more microporous. It was found that in some kinds of coal the microporosity increases with rank (Prinz & Littke, 2005; Clarkson & Bustin, 1996). In this cases methane sorption capacity increases with rank.

In research on the influence of the petrographic composition on the methane sorption capacity of hard coal it was found that there are differences between bright and dull coals. Bright coals are vitrinite-rich, whereas dull coals are inertinite rich; the vitrinite contains as maceral, among others, the colinite and inertinite contains semifusinite. It is the semifusinite that is the chemical reactive component (Taylor et al., 1998; Mastalerz & Bustin, 1997), which follows from the chemical structure of macerals. As a result of that, the bright vitrinite-rich coals have a higher sorption capacity than dull inertinite rich of the same rank (Clarkson & Bustin, 1999; Hildenbrand et al., 2006). In contrast, inertinite rich coals of low and medium ranks were found to have higher sorption capacity than vitrinite rich coals, whereas for high rank both coals have similar sorption capacity.

In addition, the sorption capacity of coal is also influenced by such factors as: moisture content, mineral matter content.

In this paper, it was attempted to find a connection between the sorption capacity and the petrographic composition of coal samples originating from Upper Silesian Basin and Lower Silesian Basin in Poland. An analysis of methane sorption isotherms obtained previously for those coals by such authors as: (Ceglarska-Stefańska, 2000; Nodzeński, 2000; Ceglarska-Stefańska & Brzóska, 1995) was conducted.

2. Effect of maceral composition on the sorption capacity of coals originating from number of different coals basins in the World

The sorption capacity of coal is usually presented as the Langmuire volume V_L [cm³/g] depending from the vitrinite content (%) in dry coal. There were chosen three known from the literature types of those influences with respect to three coal basins, in order to better present the differences indicated in the previous point.

The first analysis concerns coal samples from the lower Permian Barkan/Karhabari Formation and from the upper part of the lower Permian Barakar Formation (India). Those dry ash free

hard coals are characterized by their high sorption capacity: 30-40 cm³/g with relatively low rank: $0,6 < R_o < 1,5\%$. They strongly differ with the vitrinite and inertinite content and lack the content of liptinite/exinite. The mineral matter, at a level of few percent, occurred to be unimportant in those research. Thus vitrinite and inertinite dominate and the coals can be considered as a two component system, therefore vitrinite content was used to characterize the coal type. Figure 1 presents a comparison of vitrinite content with sorption capacity which suggest that the two parameters are unrelated. This interesting conclusion was presented in the work (Laxminarayana & Crosdale, 2002).

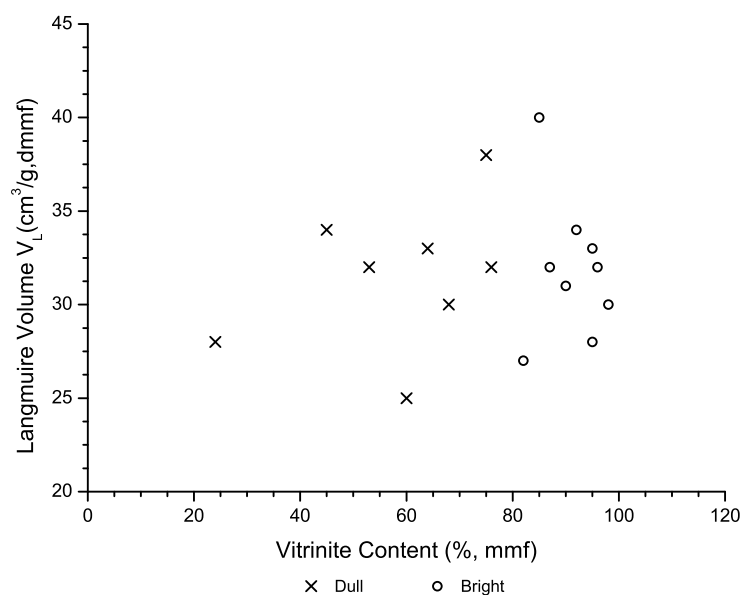


Fig. 1. Effect of maceral composition on adsorption capacity of dry coal (India)

The second analysis regards coal samples from Bowen Basin, Australia coals. Those dry ash free coals are characterized by high sorption capacity within 35-50 cm³/g and a broad scope of changes of rank: $0,5 < R_o < 3\%$ (Laxminarayana & Crosdale, 1999) and lack the content of liptinite/exinite and have varying contents of mineral matters. It was adopted that their system is two component. The content of vitrinite was this the feature characterizing those types of coals. Figure 2 presents the relation of Langmuire's sorption capacity to the content of vitrinite (Laxminarayana & Crosdale, 1999).

One can notice a complex nature of this relation. In the low rank coals the increase of content of vitrinite causes also the increase in the sorption capacity. In medium to high rank coals, changes in the maceral composition have rather little influence on the sorption capacity of those coals. A similar observation on the minimalization of the influence of changes of maceral contents regards also the coals of a high rank but no semianthracites.

The third analysis concerns the results of the research of hard coal samples from locations within North America (Chalmers & Bustin, 2007). The coals have the values of methane sorp-

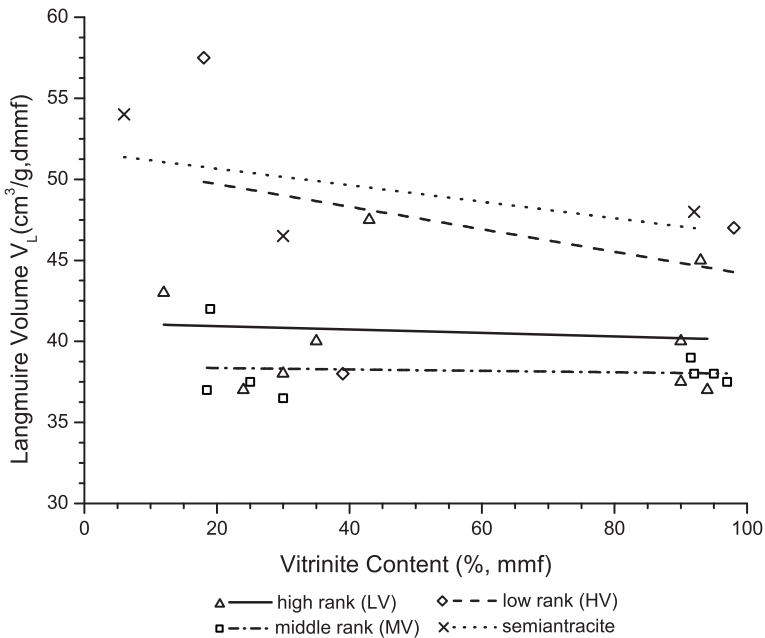


Fig. 2. Effect of coal type on adsorption capacity of dry coal (Australia)

tion capacity in a broad scope of changes 5-25 cm³/g with also a broad scope of change of rank: $0,6 < R_o < 4\%$ (coal dry, ash free). The presence of mineral matters in the examined coals did not turn out be material, theris system may be assessed as two component. In the broad scope of changes of values of inertinite and vitrinite a particular focus was placed on the differences in results of those researched within bright and dull coals, however the number of coal samples was rather small. The quite important role of presence of telovitrinite next to vitrinite in the macerals was notices. This is illustrated by Figure 3, which present a positive relationship between both vinitrinite and telovitrinite contents with the methane sorption capacity.

Foremost however, on this figure the lower situated data points are from the low rank (high volatile coals – HV) and higher data points are high rank (low volatile coals – LV). In the more in-depth analysis it was noticed that the dull samples can have higher methane sorption capacities than bright samples of a lower rank and bright samples have a higher mathane sorption capacities than dull samples of a higher rank. The difference in methane capacity between bright and dull ones increases with rank. From the presented analysis there follows a quite complex nature of the examined relation. The question rises, what is this relation for the Polish hard coals?

3. The maceral content and methane sorption capacity of dry coals (Poland)

For the purposes of analysis fourteen samples of coal, including nine taken from the Upper Silesian Basin and five from the Lower Silesian Basin, were chosen.

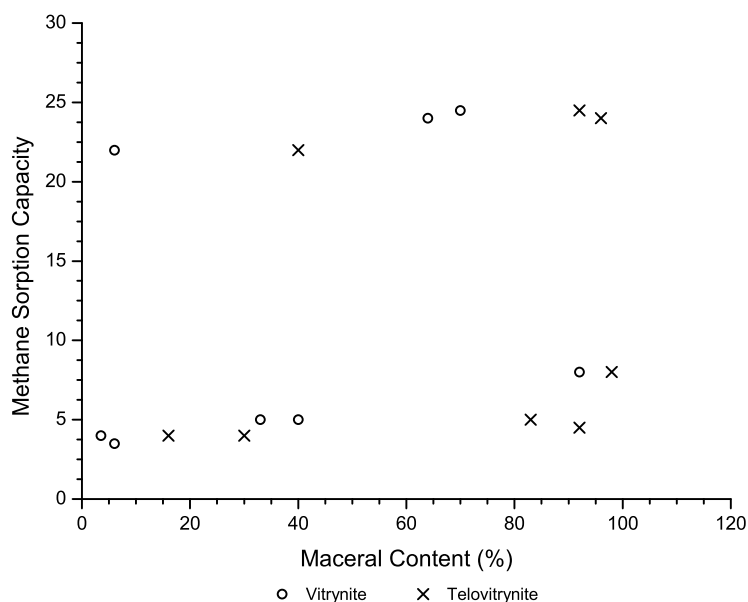


Fig. 3. Effect of maceral content on methane sorption capacity of dry coal (North America)

The results of the examination of isotherms of methane sorption on those coals and the results of the petrographic analysis of those coals obtained previous by various authors, mainly (Celgarska-Stefańska, 2000; Nodzeński, 2000; Ceglarska-Stefańska & Zarębska, 2000), were used. Moreover, the results of other works were also used (Ceglarska-Stefańska 1990; Nodzeński, 1998).

The level of macerals in those coals is presented in Table 1.

TABLE 1

Maceral Component (%)

Sample	Vitrinite	Inertinite	Exinite	Mineral Matter
A	7,4	66,9	19,8	5,9
B	45,9	40,0	3,6	8,8
C	49,2	32,4	12,5	5,0
D	50,0	35,4	11,2	2,8
E	55,5	38,4	0,0	3,9
F	56,1	31,8	4,9	3,1
G	56,1	19,1	18,8	2,0
H	60,7	27,5	9,6	2,2
I	61,6	16,6	18,6	3,0
J	61,6	32,8	0,0	4,2
K	67,5	14,8	10,8	6,5
L	72,0	23,6	-	-
M	75,0	16,1	2,6	6,3
N	76,4	7,2	13,6	2,8

Among the analyzed coals the high volatile coals (HV) prevail. There are such coals as H coal of medium mineral matter content with very small grains, which are dispersed among macerals. The important maceral is fusinite present as a variation of pirofusinite and gradofusinite in this coal. In the pore structure of those components there are high volumes of mezo and macropores. To this type of coals belong also coal C, in which the semifusinite is present in high volumes along with micrinite. This coal considerable microporosity which is connected with its sorption capacity. In this group of coals a partial attention is focused on coal A which has a very high value of content of inertinite and a little volume of vitrinite. Inertinite is represented evenly by semifusinite and inertodetrinite and also important in the composition is exinite/liptinite. Quite high is also the volume of mineral matter. The mezo-macroporosity of this coal is high and the microporosity is low. A considerable amount of inertinite is also present in coal F with a noticeable macroporosity.

Similar high volume of inertinite contain middle volatile (MV) coals: B, D and J. Coal B is characterized by a high amount of mineral matters and coal D has a high volume of the elementary coal.

Coal K does not differ from the other coals in Table 1, but has interesting sorption capacity, which will be presented below.

Coal E is semianthracite and coal N anthracite with a considerable volume of vitrinite. In porous space of this coal a high microporosity is noticeable.

4. Analysis of methane sorption capacity of dry coals (Poland)

For the examination of the sorption capacity of chosen coal there were used the high-pressure sorption isotherms, which were previously obtained mainly in the works of such researchers as (Ceglarska-Stefańska, 2000) and (Nodzeński, 2000). For the description of those isotherms the Langmuire equation can be used in the following form:

$$V = \frac{PV_L}{P_L + P}$$

or in the linear form:

$$\frac{P}{V} = \frac{P_L}{V_L} + \frac{P}{V_L}$$

Where V is the volume of adsorption gas at pressure P , V_L is Langmuire volume, P_L is Langmuire pressure. V_L physically represents the monolayer adsorption capacity and P_L is related to the heat of adsorption capacity and may give some information about the heterogeneity of the pores. The structure of porous space has, as can be seen, an important meaning for the discussed issues.

The isotherms of sorption in the nonlinear relationship $V(p)$ differ a little from one another for samples of coal from the Lower Silesian Basin, with perhaps the exception of coal J and reach the half of their equilibrium value already at the pressure of approximately 3,5 bar and for coal E this pressure is even lower.

Achieving a linear relation $V_1(P)$ in the scope of $0 < P < 80$ bar of those coals was not troublesome.

The adsorption isotherms of the samples from the Upper Silesia Basin were made within the pressure $0 < P < 45$ bar. Some of them, e.g. for coals A, H, M are similar to one another and have a shape of a line that does not differ from slopes. Other isotherms, e.g. for coals C and J are more inclined in this scope of pressures. The high inclination of the curvelinear isotherms regards coal K, and the biggest one regards coal N. Laying out straight-linear relation $V_L(P)$ raised some issues only with respect to coal K and coal F.

The obtained values of methane sorption capacity V_L were presented in a Figure 4 in relation to the volume of vitrinite, that is depending on the type of coal.

The material majority of the points is concentrated in a rather narrow, vertical band along the axis of vitrinite content (7-76%), except of coal K and anthracite. This it can be considered, that for those coals methane sorption capacity and vitrinite/inertinite content are unrelated. As a value of sorption capacity representing those coals $23 \text{ cm}^3/\text{g}$ can be assumed. Higher values from this on is possess by coal K and anthracite N. Seminathracite E, perhaps unexpectedly, has a lower methane sorption capacity because his vitrinite content is small. It can be noticed, that there are some analogies from the comparison of results presented in the figure 4 with those presented on figure 1 which regards Indian coals.

In the presented analysis the problem of reation between methane sorption capacity and coal rank (vitrinite reflectance) was not considered.

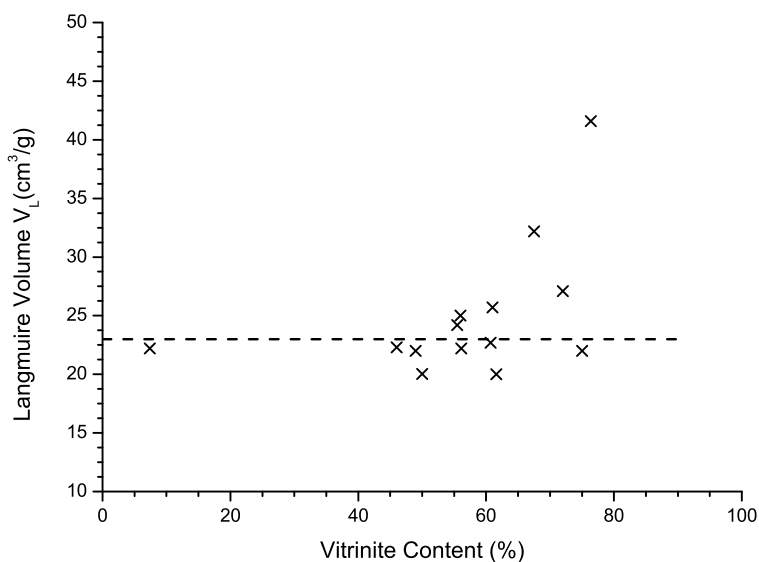


Fig. 4. Methane sorption capacity of dry coal and the maceral content (Poland)

5. Summary

The type of coal in terms of content of macerals has little influens on the sorption capacity of methane in the examined samples. This capacity is not materialy related to the share of vitrin-

ite and share of inertinite in the coal. This regards mainly to high and medium volatile coals in a dry state, but no to anthracite. Similar results to ones presented in this paper are known in the literature, e.g. with respect to Indian and partially to Australian coals.

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