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Sorption of Water Vapour on Exinite Concentrates

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Abstract. Maceral concentrates of the exinite group, isolated from the hard coals from the Janina and Brzeszcze Mines were studied. Sorption studies in the coal-water vapour system and the concentrates maceral-water vapour system were carried out using the volumetric method (under isothermal-isobaric conditions) at 298 K, at the following relative sorbate pressures: 0.19; 0.34; 0.52; 0.70 and 0.88.

The presented sorption isotherms show that the exinites isolated from coals have higher water vapour sorption capacities than the coals from which they were isolated. Their sorption capacity is closely related to the accessibility of their porous structure during the interfacial-volumetric process of water vapour interaction in the coal substance.

Keywords: sorption of water vapour, coal, petrographic constitution

Introduction

Considerations of interactions between coals and low molecular substances address the question what is the influence of petrographic composition of the coal on its heterogeneity in sorption processes. To answer this question the investigations have been initiated in the Faculty of Fuels and Energy of the University of Mining and Metallurgy (Cracow). They are focused on studies of the behaviour of macerals concentrates, separated from the coals of various degree of metamorphism, during sorption of water vapour. The first stage of studies, devoted to the sorptive properties of the vitrinite concentrates, isolated from the flame coal and the gas-coking coal was described in (Ceglarska-Stefańska and Brzóska, 1993).

The water vapour sorptive capacity of hard coals is determined primarily by the nature of their surface "phase". The regions of sorption, at which the specific inter-particle interactions appear, are the greatest in vitrinite and exinite concentrates. For this reason the second stage of the studies was performed on exinite concentrates isolated from the low rank coals, as exinite transform to vitrinite in the coals ($V^{\mathrm{daf}} < 22$–18%) of a higher rank (Gabzdyl, 1987). The exinite group consists of macerals formed from the substances of a vegetable origin, resistant to decomposition. Exinite occurs in the semi-dull and semi-bright coals mainly. It is a component of the lowest degree of carbonification, of the highest content of volatile substances and of the least ordered structure (Jasieńko and Kidawa, 1986). The low degree of order in exinite structure and the presence of a relatively high content of aliphatic and alicyclic systems were confirmed by X-ray analysis (Jasienko and Kidawa, 1986).

The process of sorption may be considered both as the dynamic and the static one. The dynamic characteristics, most commonly used in dynamic investigations is so-called sorption kinetics, denoting the relationship of sorption capacity on time, at the abrupt change of pressure. The basic static characteristic of the process is its sorption isotherm, showing the relationship between the equilibrium sorption capacity upon sorbate pressure, at constant temperature.

Sorption methods are applied in fundamental studies to define the porous structure of coals and their dilatational properties (Ceglarska-Stefańska and Czapliński, 1993; Ceglarska-Stefańska, 1993) as well as to analyze the correlations between coal sorptive properties and its petrographic and chemical composition. The coal sorptive capacity, kinetics of sorption and desorption and sorptive deformation of coals under the influence of vapours and gases are important in coal mining and processing. The above mentioned factors affect the mechanical resistance of coal, determined also by its carbonification, petrographic constitution, and the type and number of fissures. Our empirical results give the comparison of the water vapour sorption capacity of “raw” coals (Ceglarska-Stefańska and Czapliński, 1993; Ceglarska-Stefańska, 1993), vitrinite concentrates (Ceglarska-Stefańska and Brzóska, 1993) and exinite concentrates.

Experimental

Maceral concentrates of the exinite group, isolated from the coals from the Janina Coal Mine (denoted with the symbol E-J) and the Brzeszcze Coal Mine (denoted as E-B) were studied. The petrographic components were separated by concentrating in heavy liquids (the mixture of tetrachloromethane and xylene), using the previously separated lythotypes. The results of chemical and technical analysis of the samples studied is given in Table 1, while their petrographic composition—in Table 2. Both Tables contain also data on the coal samples (J, B), from which the studied exinite concentrates were isolated.

The sorption investigations were carried out using the volumetric method, presented earlier many times. The method applied allows to observe the changes in sorptive capacity of the studied samples under isothermal-isobaric conditions. The investigated coal samples were degassed down to 1×10^{-5} Pa and rinsed with helium several times. The measurements were carried out at 298 K. The kinetics of the water vapour sorption on exinite concentrates was determined at the following relative pressures of sorbate: 0.19; 0.34; 0.52; 0.70 and 0.88. The real density of the studied material was determined using the Accu Pyc 1330 apparatus, produced by Micromeritics. The low values of this parameter observed for exinite concentrates are consistent with the published data (Jasieńko and Kidawa 1993; Jasieńko and Róg, 1995).

Table 1. Characteristics of samples studied.

Parameter	J[a]	B[a]	E-B	E-J	W-J
Ash (wt%)	2.6	8.2	1.47	1.8	2.4
Volatile matter (wt% daf[b])	39.2	29.3	48.2	35.8	37.99
C (wt% daf[b])	75.2	84.2	82.3	72.6	71.8
H (wt% daf[b])	5.0	4.68	5.57	4.2	4.01
(O+N) (wt% daf[b])	15.67	10.67	0.67	0.93	13.6
True density ($g \cdot cm^{-3}$)	1.62	1.36	1.20	1.18	1.35
Porosity (%)	7.4	3.2	—	—	—

[a] Polish classification, international classification: J: 31, 700-800; B: 32.2, 722-721.

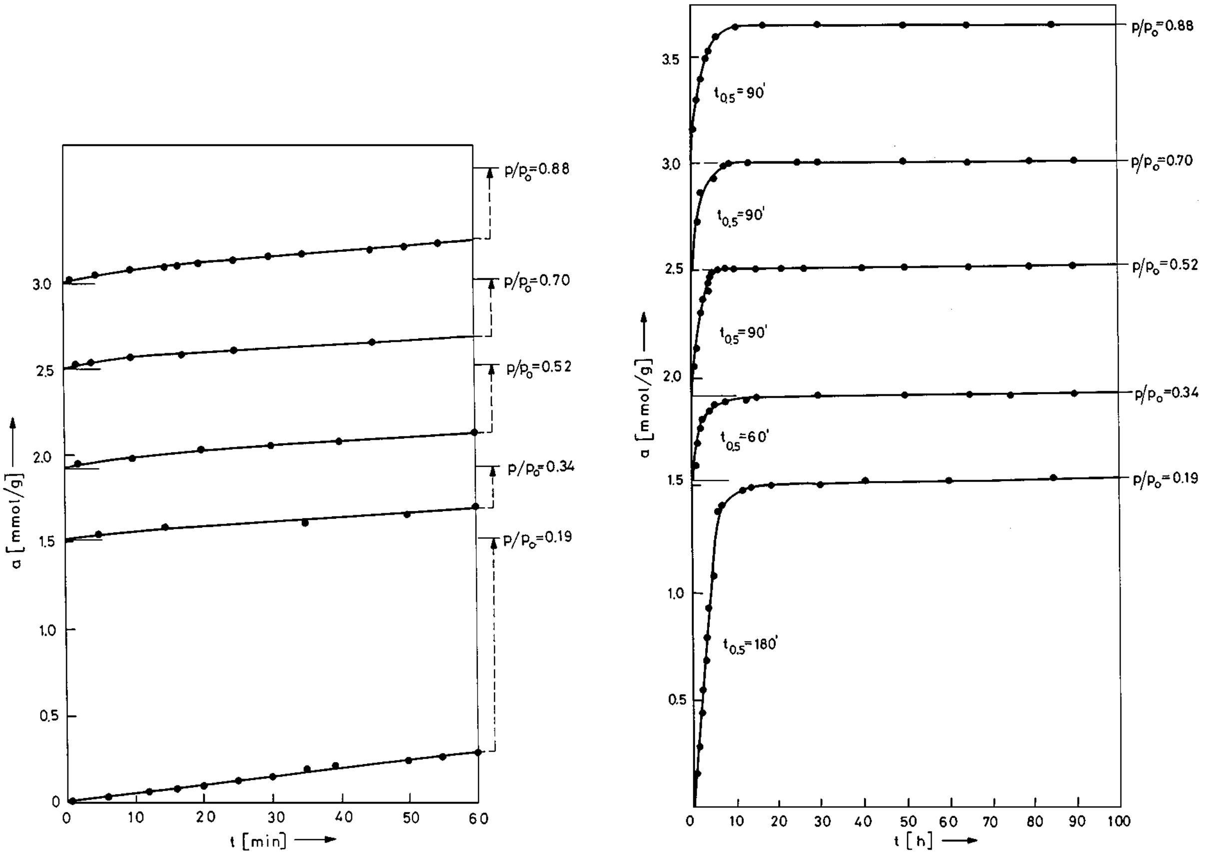
[b] daf—dry and ashless state.

Table 2. Petrographic analyses of exinite concentrates and coals studied.

Group of macerals	Maceral and its symbol	E-J	E-B	B	J
		Contents (%)			
Vitrinite	Tellinite	1.1	0.0	—	0.4
	Collinite	4.8	6.1	7.4	69.0
	Vitrodetrinite	—	—	—	—
Sum		5.9	7	7.4	69.4
Exinite	Sporinite	84.4	81.7	13.9	8.0
	Cutinite	0	0.6	1.1	—
	Resinite	2.0	2.2	4.8	0.9
	Alginite	—	—	—	—
Sum		86.4	84.5	19.8	8.9
Inertinite	Micrinite	0.9	2.1	7.4	1.0
	Macrinite	0.9	0.5	0.7	0
	Semi-fusinite	4.7	4.0	30.2	12.1
	Fusinite	1.2	1.3	1.3	7.0
	Sclerotinite	—	—	1.9	0.5
	Inertodetrinite	—	—	25.3	0
Sum		7.7	7.9	66.9	20.6
Mineral substance		—	0.6	5.9	1.1
Total sum		100	100	100	100

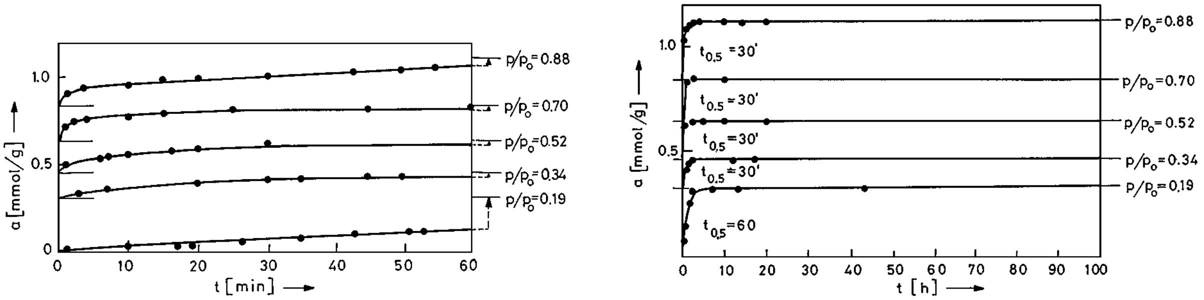
Results and Discussion

The results of investigations are presented in the form of graphs showing the relationship between the sorbed amount of water vapour and time (Figs. 1 and 2). They were used in calculations of the time relationship of the relative sorption values, $\alpha = a_t/a_{\max}$. From these relationships the half times of sorption saturation, t were found and used in estimations of the diffusion parameter, D_e/R^2 . The latter was calculated with the



(a) (b)

Figure 1. Kinetics of water sorption of exinite concentrate E-J in studied range of relative pressures: (a) minute scale and (b) hour scale.



(a) (b)

Figure 2. Kinetics of water vapour sorption of exinite concentrate E-B in studied range of relative pressures: (a) minute scale and (b) hour scale.

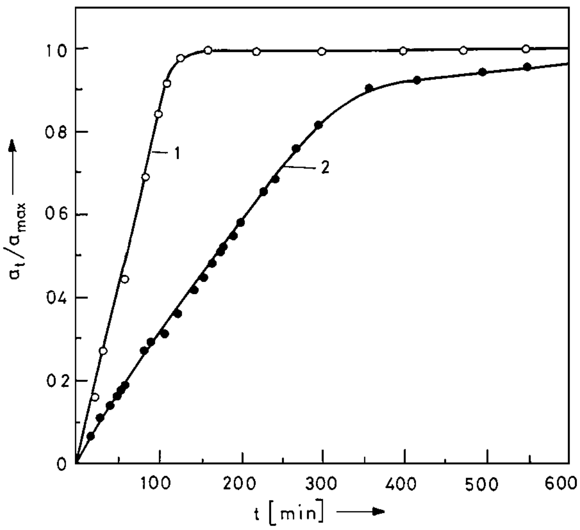


Figure 3. Kinetics of water vapour sorption both of concentrates at $p/p_0 = 0.19$: curve 1—E-B; curve 2—E-J.

Timofieyev formula (Timofieyev, 1962):

$$D_e/R^2 = 0.308/\pi^2 t_{0.5}$$

where R is the radius of an equivalent circular diffusion area, containing only the smallest pores, which limit the diffusion rate. The relative sorption values ($a_t/a_{\max}$), at fixed time intervals, (t-min), determined under defined experimental conditions, are the simplest measure of water vapour sorption capacity. The time course of the relative sorption values for the water vapour relative pressure, $p/p_0 = 0.19$, is presented as an example (Fig. 3). A relatively fast diffusion was observed for the exinite concentrate isolated from the coal B, over the whole range of relative pressure values. Thus, as the first approximation it may be assumed that this coal has the system of pores which is more easily accessible for the sorbate molecules.

The relationship of the diffusion parameter D_e/R^2 on the sorbate relative pressure, and thus on the degree of filling of the concentrates studied is increasing up to $p/p_0 = 0.34$ (Fig. 4). The maximum observed for the sample E-J may be explained by a change of sorbate transfer mechanism in coal pores. It is consistent with the published data (Kawęcka, 1994), indicating that the more significant is the eventual maximum, the lower is the coal carbonification (Table 1). Similar computations carried out for the vitrinite concentrate isolated from the coal J also gave the maxima, although they were occurring at higher degree of filling (for $p/p_0 = 0.6$) (Ceglarska-Stefańska and Brzóska, 1993). This effect may be related to the physical and chemical structure of macerals. Petrographic components of coals: vitrinites, exinites, micrinites and fusinites differ in the elemental composition and structure. Particularly characteristics are differences in the contents of carbon, hydrogen and oxygen. Carbon content is usually the highest in fusinites and the lowest in vitrinites. Hydrogen content is the highest in exinites and the lowest in fusinites. The oxygen content is the highest in vitrinites. Also the contribution of aliphatic hydrogen contained in methylene groups, H_{CH_2}/H_{aliph}, changes in a characteristic way: it is the highest in exinite (0.7–0.5), then followed by vitrinite (about 0.5) and micrinite and semifusinite (0.36) (Majchrowicz et al., 1987). A significant part of aliphatic materials is located in hydroaromatic structures. Accessible data on the oxygen containing groups of the petrographic components are not consistent, but it may be stated that the total oxygen content decreases in the following order: vitrinite-micrinite-exinite-fusinite. The total content of oxygen and the content of —OH groups in macerals diminishes with carbonification. It is difficult, however, to describe the content of carbonyl groups in particular macerals in a more precise way.

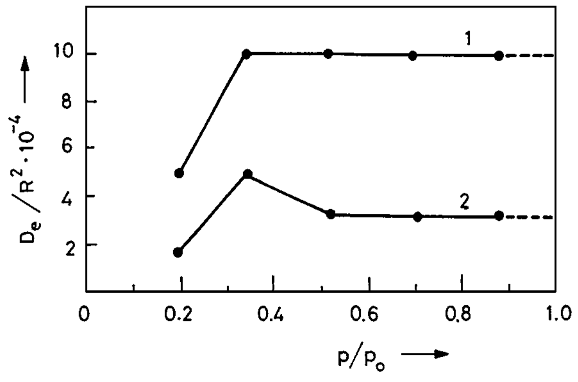


Figure 4. The relationship of the diffusion parameter D_e/R^2 on the sorbate relative pressures: curve 1—E-B; curve 2—E-J.

The other reactive oxygen groups such as —OCH_3 and —COOH were found in low rank flame coals. The coal containing 81.5% C did not contain —OCH_3 group (Jasieńko, 1995). The content carboxylic oxygen did not exceed 1.5% in these coals. Any unquestionable description of the sorption dynamics in materials of the structure so complex as hard coals is very difficult, because several phenomena proceed simultaneously. They are: molecular diffusion, resulting from the fast transport of sorbate particles through big macro- and mesopores, much slower movement of sorbate particles through micropores, with periodical stopping of the particles on the surface and diffusion within the elastic phase of carbon copolymer. The presence of the third mechanism is indicated by results of sorptive deformation of coals (Ceglarska-Stefańska and Czapliński, 1993; Ceglarska-Stefańska, 1990, 1993) and theoretical models of the process of sorption in the coal—the low molecular substance systems (Milewska-Duda, 1993, Milewska-Duda and Duda, 1993).

The current knowledge on the mechanisms of sorbate molecules deposition in hard coals allows to assume that the sorptive processes are of the adsorptive-absorptive nature, determined by the change of geometrical parameters of the system. The reduction of the diffusion parameter observed for higher fillings of the coal E-J results from the third, slowest mechanism—the process of water molecules penetration into the smaller and smaller pores as well as into new areas, formed due to the sorptive deformation of macro- and molecular elements of the coal matrix of exinite (Milewska-Duda, 1993; Milewska-Duda and Duda, 1993; Milewska-Duda et al., 1994). The results of X-ray studies, carried out on Polish hard coals (Jasieńko and Kidawa, 1993) indicate that the degree of structure order is low in exinites. A big part of their structure consists of nonaromatic systems (aliphatic and alicyclic).

The contribution of nonaromatic systems in petrographic components of the definite coal diminishes in the following order: exinite-vitrinite-micrinite-fusinite. It also decreases with the degree of coal carbonification, particularly significantly in macerals of exinite and vitrinite. The molecular compounds in the coal structure form the elastic sorptive layer during sorption processes. Moreover, the considerable part of hydrogen present in the coal substance is bound to the aromatic rings. The contribution of aromatic hydrogen in exinite does not change significantly, while passing from the flame coal (type 31) to the gas-flame one (type 32.2). However, this contribution increases considerably in vitrinites. As it was previously mentioned, the petrographic components differ also significantly in the content of groups containing oxygen, responsible for the specific interactions in the coal-water vapour system. The considerable part of the compounds containing oxygen in vitrinites and exinites are phenolic hydroxyl groups, present in minor quantities in fusinites and micrinites. The oxygen ether groups are a considerable part of exinites and vitrinites of flame coals and much smaller part of the respective micrinite. Jasieńko (Jasieńko and Kidawa, 1993) suggests that vitrinites and micrinites contain much more oxygen in the heterogenic form than the corresponding exinites.

The above mentioned properties of various groups of macerals, determined by the degree of their carbonification affect significantly the results of sorption studies presented in the form of the relationship between the sorbed water vapour and the equilibrium pressure. The respective water vapour sorption isotherms, obtained for exinites E-J and E-B, for the vitrinite concentrate, isolated from the coal J as well as for the raw coal J and B (Ceglarska-Stefańska, 1993), are shown in Fig. 5. Considerable differences in sorption capacity of the studied samples are consistent with the common

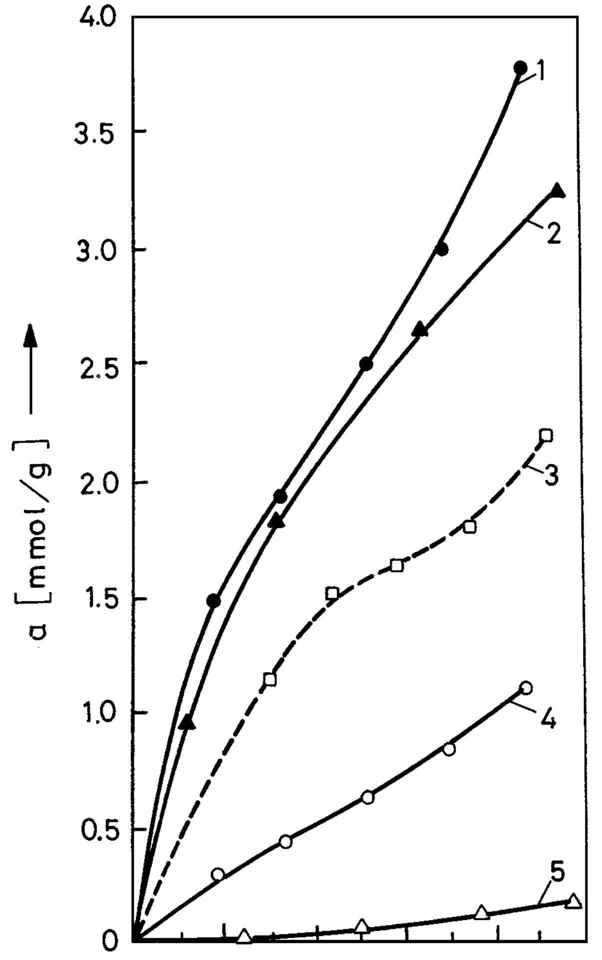


Figure 5. Isotherms of water vapour sorption: (●) 1—exinite concentrate E-J; (▲) 2—“raw” coal J; (□) 3—vitrinite concentrate W-J; (○) 4—exinite concentrate E-B; (△) 5—“raw” coal B.

opinion that water vapour sorption is a good method of differentiation between various hard coals. This fact remains in a close relation to the physical and chemical structure of coals and their petrographic forms, changing with the increasing content of carbon, molecular compounds and the presence of oxygen groups, as well as with the increasing order of the structure.

Analysis of the kinetic data and water vapour sorption isotherms in the region of small filling, shows that sorption takes place mainly on the accessible adsorption centers, where water molecules are adsorbed specifically. After filling these centers (with the adsorbed molecules) there remains a free sorption space, which is filled up due to dispersive forces. The mutual interactions of particles and adsorption centers are added to the dispersive forces, resulting in the increase of adsorption energy. As the hard coals have no rigid structure (dilatation observed was described in (works of Ceglarska-Stefańska and Milewska-Duda)) it cannot be assumed that the limiting adsorption volume is constant. Also the surface of copolymer is neither homogeneous nor smooth. Macroparticles form a spatial lattice system and the molecular part form a second phase, located in the pores of macromolecular lattice. Depending on the degree of metamorphism of particular coals, water particles either specifically interact through oxygen containing groups, present in pores or wedge themselves between the interfacial groups and molecular compounds, which pushes them apart and causes elongating of aliphatic and alicyclic chains. It leads to increase of distances between the lattice macromolecular systems (dilatation of submicropres), i.e., swelling of the coal matrix. This effect is particularly clearly visible in exinite concentrates (Fig. 5), for the samples of a relatively high content of aliphatic derivatives (the elastic phase of the coal copolymer), an unordered structure and the lowest content of the condensed aromatic derivatives (Li Fan et al., 1995). These factors cause that exinites have the most mobile structural elements and the highest sorptive capacity towards water vapour of all petrographic components of coals. The limitation of the mobility of structural elements increases with the degree of carbonification, in all groups of macerals. It is reflected by the run of water vapour sorption kinetics during the initial periods of the contact between the sample and sorbate (Figs. 1(a) and 2(a)) and by the values of $t_{0.5}$. The same effect is revealed while observing the change from exinite to fusinite, isolated from the same coal. This regularity is approximately illustrated also by the water vapour sorption isotherms, determined for the raw coal B (containing so much as 30.2% of semifusinite (Table 2)) and for exinite isolated from this coals (E-B) (Fig. 5). Water particles, adsorbing at the first adsorption centers are strongly deformed and may form a basis for formation of the water associates, having no possibility to overcome the barrier of mobility of the coal substance. At this step the isotherms observed are of the type characteristic for any hydrophobic surface (B).

It is commonly accepted that the most uniform and therefore the most representative maceral of hard coals is vitrinite (Jasieńko and Kidawa, 1986). Therefore, the isotherm of water vapour sorption on this maceral (W-J, 95% vitrinite), isolated from the coal J was presented as an example (Fig. 5). The observed reduction of the sorption capacity of W-J most probably results from the diminution of the accessibility of a porous structure for the penetrating molecules, caused by some reduction of molecular derivatives.

The presented results are complementary to the description of the mechanism of the location of sorbate molecules within the coal substance, as it was already mentioned in our recent paper (Ceglarska-Stefańska and Brzóska, 1993). It seems that the percentage of different groups in macerals should be taken into account at determinations of structural parameters for raw coals, basing on the sorption studies.

The presented sorption isotherms indicate that exinites are the most reactive components in the process of the water vapour sorption on the low rank coals. It is closely related to the accessibility of their structure during the interfacial-volumetric process of water vapour sorption in the coal substance.

Nomenclature

E-J	Concentrate of exinite isolated from coal J
E-B	Concentrate of exinite isolated from coal B
J	“Raw” coal
B	“Raw” coal
W-J	Concentrate of vitrinite isolated from coal J
p/p_0	Relative pressure
a_t	Sorption value after time t
$a_{\max}$	Sorption value at equilibrium state
$a_t/a_{\max}$	Relative sorption value
$t_{0.5}$	Half time of sorption saturation
D_e/R^2	Diffusion parameter
R	Radius of an equivalent circular diffusion area, which limit the diffusion rate
daf	Dry and ashless state

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