POROUS STRUCTURE AND TRANSPORT PROPERTIES OF A CARBONIZED PHENOLIC RESIN

Pavel FOTT, Frantisek KOLAR and Zuzana WEISHAUPTOVA

Institute of Rock Structure and Mechanics,
Academy of Sciences of the Czech Republic, 182 09 Prague 8, The Czech Republic

Received May 16, 1994
Accepted October 31, 1994

On carbonizing phenolic resins, the development of porous structure takes place which influences the transport properties of carbonized materials. To give a true picture of this effect, specimens in the shape of plates were prepared and carbonized at various temperatures. The carbonizates obtained were studied by adsorption methods, electron microscopy, and mercury porosimetry. Diffusivities were evaluated in terms of measuring the kinetics of wetting and drying. It was found out that the porous structure of specimens in different stages of carbonization is formed mostly by micropores whose volumes were within 0.06 to 0.22 cm^3/g. The maximum micropore volume is reached at the temperature of 750 °C. The dependence of diffusivity on the carbonization temperature is nearly constant at first, begins to increase in the vicinity of 400 °C, and at 600 °C attains its maximum. The experimental results reached are in agreement with the conception of the development and gradual closing of the microporous structure in the course of carbonization. The dependence of diffusivity on temperature can be expressed by the Arrhenius equation. In this connection, two possible models of mass transport were discussed.

Highly cross-linked polymers are used as precursors of isotropic non-graphitic carbon materials[1]. The initial substance is a liquid resin (most often a phenolic resin – resol or polyfurfuryl alcohol) from which a gel is formed at first by curing on gradual increasing the temperature and finally a glasslike polymer in the form of a compact solid body. In subsequent carbonizing, a carbonaceous material is obtained whose properties depend to a large extent on the carbonization conditions. The dominant influence on these properties has the final temperature of carbonization – HTT (heat-treatment temperature[2,3]).

On carbonizing to temperatures around 1 000 °C, a glassy carbon is prepared which is solid, hard, thermally stable and chemically resistant[1–5]. It exhibits small open porosity and therefore also small permeability for gases and sorption capacity. The glassy carbon is used as a material for preparing crucibles, medicinal prosthetic materials, electrodes, etc. On the contrary, by carbonizing to lower temperatures (600 – 800 °C), a microporous material[2,3], characteristic of molecular sieves with relatively high sorption capacity, is obtained. This type of material has been recently tested with success even as a highly selective membrane for separating gases[6,7]. The condition of the successful separation is the absence of larger holes and cracks in the material.

In the course of carbonization, the properties of material change owing to the chemical reactions connected with evolving the pyrolysis gases[2,3,8,9]. In addition to their main component – water vapour – carbon oxides, methane and hydrogen are evolved, too. A mass loss, an increase in carbon content and a volume contraction take place during the process, which, however, are not connected with a change in the specimen shape. Literature presents a number of examples of dependences of the properties of carbonizates on HTT (refs[2,3,8,10]). Especially density, mechanical properties (modulus of elasticity, ultimate strength) and conductance are concerned.

The information on the development of porous structure during carbonization is less numerous: By the SAXS method, the occurrence of pores of dimension 2.5 nm was found out which could be clearly observed beginning at the temperature of 500 °C, and with further increase in temperature, neither their dimension nor their total porosity (about 30%) changed[2] any more. The adsorption measurements of vapours with molecules of different size proved[3] that the prevailing part of orifices of these micropores lies within 0.4 to 0.5 nm. The maximum sorption capacity was attained at the temperatures around 700 °C when majority of pores was open. The following decrease gave evidence of a gradual closing of microporous system, this process having been finished approximately at 1 200 °C. With the porous structure are connected even the transport properties of carbonizates (permeability, diffusivity): the higher is the porosity and pore size the more favourable are conditions for transport of gases. It is well-known that the permeability of the initial cured polymer (resite) and the resulting glassy carbon is very low. However, the data on the development of permeability in the course of carbonization are, with an exception[6], missing.

The carbonization of specimens from resite and similar glassy polymers has to take place sufficiently slowly, otherwise the specimen damage and the crack formation take place. A so-called critical heating rate[11] depends on the wall thickness: for instance, for a plate of wall thickness 4 mm, the critical rate is already very low, 4 K/min (ref.[11]). The specimen damage can be explained by its stress owing to an excessive increase of pressure of pyrolysis gases inside the specimen. The value of this overpressure depends especially on the rate of generation of gases and consequently on the heating rate, on the wall thickness (for the given geometry) and on the permeability. Slow heating which is required especially with bulky specimens is connected with relatively low values of the permeability of carbonized specimen.

Recently we have suggested a mathematical model of carbonization of resite[12], based on calculating the gas pressure inside the specimen in the course of carbonization and discussed the possibility of application of this model for determining the optimum regime of preparing the glassy carbon. The numerical solution of this optimum regime requires three types of data: kinetic parameters (kinetics of carbonization), adequate description of gas transport including the expression of the diffusivity values under the conditions of carbonization and the experimental data on the conditions of crack origin. The most difficult task is the solution of problem of gas diffusion inside the specimen whose structure is being developed in the course of carbonization. With regard to the changes of structure (development and/or closing of pores), it is possible to expect not only non-constant values of transport parameters, but also the fact that a change of mechanism of gas transport is not to be excluded during the transformation of polymer precursor to the microporous carbonaceous substance.

The aim of this paper is to give a true picture of transport properties of carbonized specimens with respect to the changes in porous structure in the course of carbonization and so to contribute to the solution of the problem formulated in the foregoing paragraph. The judgement of the suitable mechanism of gas transport in the material carbonized to different degree and determination of the dependence of diffusivity on HTT can be, moreover, a contribution also from the point of view of potential applications of polymer precursors for the preparation of microporous carbonaceous membranes.

EXPERIMENTAL

The resite specimens in the shape of a plate of dimensions 80 × 20 × 2 mm were prepared by thermal curing the resol resin UMAFORM M (UMA, Pardubice). The resin was poured into a glass mould of the shape of plate and polymerized at the temperature of 70 °C for 24 h. The gelified intermediate product was taken out of the mould and cut to the plates of the dimensions given above which were cured at the temperature rise of 5 K/h up to the temperature of 150 °C (with 2 h halt at this temperature).

The specimens at different stage of carbonization were prepared under the conditions of a linear increase of temperature 20 K/h. This value is under the critical heating rate which for the used plate of thickness 2 mm amounts to 30 K/h (ref.[11]). The carbonization was carried out in a temperature-programmed oven in a nitrogen stream (40 l/h). After reaching the final temparature, the samples were cooled at a rate of 100 K/h. In this way, the specimens were prepared carbonized at these final temperatures of carbonization (HTT): 150 °C (initial resite), 400, 500, 600, 750, 850, and 950 °C.

To study the transport properties of specimens at different stages of carbonization, the experiments were carried out based on the examination of the specimen mass on wetting and drying. The specimens dried up in a drier at the temperature of 130 °C down to a constant mass were placed in a desiccator in the medium of the defined relative humidity 100 and 44% at the laboratory temperature about 20 °C. This humidity was ensured by placing the specimen above the level of water or saturated aqueous K_2CO_3 solution. After establishing the adsorption equilibrium, the plates were dried at 130 °C.

The apparent density was determined by hydrostatic weighing of specimen in water, the true density pycnometrically in methanol (grain size below 0.1 mm). No mass increase of weighed specimen was observed during the hydrostatic weighing. The porosimetric measurements were carried out with lump specimens by means of a high-pressure Carlo Erba POROSIMETER 2000 in the pressure range of 0.1 to 200 MPa, which corresponds to the range of pore diameters from 7 500 to 3.7 nm.

The adsorption measurements were carried out by means of a Carlo Erba SORPTOMATIC 1800, using nitrogen at the temperature of −196 °C and carbon dioxide at the temperature of 25 °C as adsorbates. In the measurements with nitrogen, in some cases in addition to the adsorption branch, also the desorption one of the isotherm was measured. For the adsorption measurements, the sample of grain size below 0.1 mm was used.

For the observation of macropores in resite and in carbonizates, the electron microscopy (TESLA BS-301) was used. The analysis was carried out on the fracture surfaces of resite and carbonizates which were gold-plated by ion deposition in argon atmosphere.

RESULTS AND DISCUSSION

Development of Porous Structure

The pores of carbonaceous materials are usually divided into macropores ($25 < r < 7\,500$ nm), mesopores ($1 < r < 25$ nm) and micropores ($r < 1$ nm). The overall porosity ε comprising all the accessible (open) pores was determined from the true density ρ_r determined pycnometrically with methanol and the apparent density ρ_b determined by weighing the specimen immersed in water, $\varepsilon = (\rho_r - \rho_b)/\rho_r$. The results given in Table I illustrate the increase in porosity up to the temperature of 750 °C and its subsequent decrease. From the decrease of true density at temperatures above 750 °C, at practically constant value of apparent density, the closing of the pore orifices can be deduced. At the temperature of 950 °C, a considerable part of pores is already closed for the true density 1.58 g/cm^3 is only slightly higher than the apparent density 1.50 g/cm^3, however, substantially lower than the true density of graphite 2.26 g/cm^3. The dependence of apparent density on HTT is the resultant of mass loss and volume contraction[10]: At temperatures up to 500 °C, the effect of mass loss and at higher temperatures the effect of volume contraction prevails.

The occurrence of macropores, if any, was investigated by electron microscopy. Macropores of nearly spherical shape, in agreeement with refs[13,14], were observed,

TABLE I

Density and porosity values of carbonizates; ρ_r, ρ_b is true and apparent density, ε is porosity determined from these values, $w_0\rho_b$ is porosity of micropores (see Table II)

HTT, °C	ρ_r, g/cm^3	ρ_b, g/cm^3	ε, %	$w_0\rho_b$, %
150	1.36	1.29	4.5	10.1
400	1.37	1.20	12.1	9.7
500	1.38	1.19	13.8	15.3
600	1.43	1.23	13.9	22.6
750	1.84	1.48	20.4	31.6
850	1.65	1.49	9.5	23.8
950	1.58	1.51	4.7	9.0

these macropores being located mainly in the central part of specimen which occupies about two thirds of its volume. These bubble pores with radius about 2 μm were observed already in the initial resite and in the course of carbonization, their number, size, and shape did not practically changed. The proportion of these macropores in the specimen volume (porosity of macropores) amounted to 1.5% in the central part of specimen, which represents about 1% on converting to the whole specimen. Spherical macropores are not utilized for transporting gases. Other types of pores were not observed by electron microscopy. The occurrence of bubble macropores is apparently connected with the conditions of regime of the resite curing. After changing the curing regime by inserting a halt for 12 h at the temperature of 90 °C, practically no bubbles were observed any more. Also Fitzer et al.[2] did not observe the occurrence of bubble macropores in carbonizates prepared in laboratory (unlike the industrial specimens of glassy carbon). By using this modified method of curing, the specimens carbonized on HTT 275, 325, and 350 °C were prepared.

On studying the porous structure by mercury porosimetry, no mercury intrusion into the specimen was observed in case of glassy carbon (carbonizate prepared at 950 °C). This gives evidence of the absence of pores with diameter larger than 3.7 nm. In case of resite and low-temperature carbonizates, however, the following porosities were evaluated: 1.5% (resite), 2.5% (HTT = 500 °C), 1.7% (HTT = 600 °C), and 0.5% (HTT = 750 °C). The dependences of the volume of intruded mercury on pressure were nearly linear in these cases. This fact can be explained so that during the porosimetric analysis, the effect of the specimen compression is prevailing. The justification of this interpretation is discussed in more detail in ref.[15]; the compressibility of resite and low-temperature carbonizates is conspicuously greater than that of resulting glassy carbon[15]. With regard to this interpretation, the results of porosimetry in case of resite and low-temperature carbonizates were not taken into account.

Information on micropores and mesopores was obtained from the results of adsorption measurements. Examples of the measured isotherms of carbon dioxide at 25 °C for various carbonizates are illustrated in Fig. 1. The experimental data are satisfactorily expressed by the Dubinin–Radushkevich (DR) equation[16], which makes it possible to calculate the volume of micropores w_0

$$w/w_0 = \exp\,[-(A/E)^2]\ , \tag{1}$$

where w is the volume of gas in adsorbed state at fugacity f, w_o the limiting volume of adsorption space, in the first approximation identical with the micropore volume, w/w_0 is the degree of filling of this volume, E is the characteristic energy and A is the differential molar work of adsorption, $A = \boldsymbol{R}T \ln (f_s/f)$, f and f_s are the fugacities of carbon dioxide at pressure p and at the saturated pressure p_s (p_s = 6.43 MPa, f_s = 4.63 MPa).

Between the volume of micropores *w* and the adsorbed amount V_a (cm^3(STP)/g), the relation

$$w = V_a M / V_m \rho_a \ , \qquad (2)$$

holds where *M* is the molar mass of CO_2, ρ_a is its density in adsorbed state (according to ref.[17], $\rho_a = 0.889$ g/cm^3), and V_m is the volume of one mole of gas under standard conditions (22 414 cm^3(STP)/mole).

The parameters of the DR equation w_0 and *E* are given in Table II for all the carbonizates measured. The porosities corresponding to these micropores ($w_0\rho_b$) are given also

Table II
Results of adsorption measurements; w_0 is volume of micropores, *E* is characteristic energy, S_{micro} is surface area of micropores, S_{BET} is surface area determined by BET method

HTT, °C	w_0, cm^3/g	*E*, kJ/mol	S_{micro}, m^2/g	S_{BET}, m^2/g
150	0.086	4.75	245	0.5
400	0.081	8.97	282	1.1
500	0.128	9.19	453	2.0
600	0.183	9.47	652	56.5
750	0.216	9.64	774	4.8
850	0.159	10.57	587	3.4
950	0.060	7.48	197	3.0

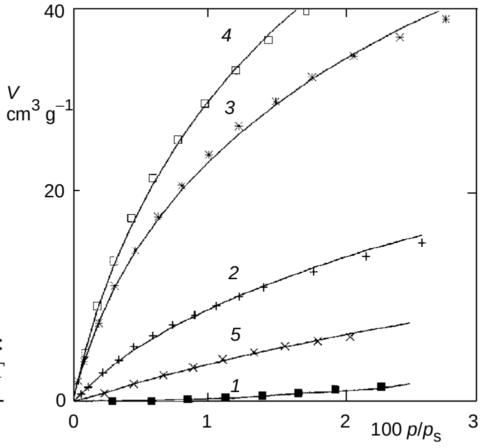

Fig. 1
Carbon dioxide adsorption isotherms at 20 °C: *1* resite, *2* HTT 400 °C, *3* HTT 600 °C, *4* HTT 750 °C, *5* HTT 950 °C. Curves represent isotherms calculated from DR equation

in Table I. Although the values of porosities determined in this way are slightly higher than the porosities calculated from the apparent and true densities, the dependences of both the porosities have a similar shape.

In addition to the micropore volume w_0, the values of specific surface area S_{micro} were also calculated by the method reported by Medek[17] (see Table II). The highest surface area is exhibited by the sample carbonized at 750 °C (774 m^2/g). The method[17] provides also the information on the mean radius $\overline{r}$ which should be related rather to the dimensions of inner space (cavities) than to the orifice of micropores. Values of $\overline{r}$ for nearly all the carbonizates (HTT = 400 to 850 °C) lay in the rather narrow interval of 0.54 to 0.57 nm, for the carbonizate HTT = 950 °C, $\overline{r}$ = 0.61 nm. For a comparison, these values are approximately half the values evaluated by the SAXS method[2] which are related to the cavity dimensions, however, approximately double than the given dimension of pore orifice[3] determined from the adsorption of molecules of various size.

In case of resite, the usual interpretation of parameters of the DR equation is to be discussed for it is not the case of a typical microporous substance. Rather than adsorption in micropores it is here the case of sorption of molecules between the chains of polymer network. The substantially lower value of parameter E of the DR equation gives also evidence of the diversity of the sorption character in resite. In the course of carbonization, this network is continuously developed into the microporous system.

From the measurement of nitrogen adsorption at the temperature of –196 °C, the specific surface area S_{BET} was evaluated by the standard method BET (ref.[16]), the resultant values are given in Table II. Values S_{BET} are very small compared to the values S_{micro}. This difference is typical of materials with a very fine porous structure (molecular sieves), this effect being exhibited by a great many carbonaceous materials including coal[18]. According to the authors[19,20], nitrogen enters, owing to the activated diffusion at the temperature of –196 °C, in finite time, only the pores with an orifice whose diameter is larger than 0.5 nm whereas carbon dioxide at the temperature of 25 °C may enter even smaller pores (including molecular sieve 4A).

The results obtained lead to the conclusion that practically all the pore volume of the resite carbonizates is formed by micropores whose maximum volume and surface area is in the vicinity of 750 °C. The decrease in values of S_{micro} and porosity at the temperatures above 750 °C can be interpreted with respect to refs[3,20] as the closing of the micropore orifices. A slightly higher value of S_{BET} for the carbonizate of HTT = 600 °C may be explained by the fact that the orifice size of a part of micropores may temporarily surpass the limit of 0.5 nm which enables nitrogen molecules to enter the micropores.

To determine the volume and distribution of mesopores, the whole nitrogen adsorption isotherm including the desorption branch was measured for the carbonizates 400 and 500 °C. The adsorption isotherm of the carbonizate of HTT = 500 °C is illustrated in Fig. 2. The hysteresis of the adsorption and desorption branch of the isotherm proves a capillary condensation in mesopores. The volume and distribution of these mesopores were determined on the basis of the Kelvin equation by the method described in ref.[21]. It was found out that the volume of mesopores of a radius larger than 1.8 nm for the carbonizate of HTT = 500 °C is equal to 0.004 cm^3/g (i.e., 2.8% of the total porosity), 90% of these mesopores having a radius lower than 5 nm, the remaining 10% of pores having radii smaller than 10 nm. In case of the carbonizate 400 °C, the same distribution was found, however, the volume of the mesopores was approximately half.

Evaluation of Diffusivities

To determine diffusivities, a method was used based on the assumption that the kinetics of wetting and/or drying can be described by the second Fick law which, for the plate geometry, takes the form

$$\frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial x^2} \ , \qquad (3)$$

where c_s (mol/cm^3) is the concentration of water in specimen, D_s (cm^2/s) is the diffusivity of water on diffusing through the solid phase, t is time and x is the length coordinate. Solution of this differential equation for lower values of the mean relative molar

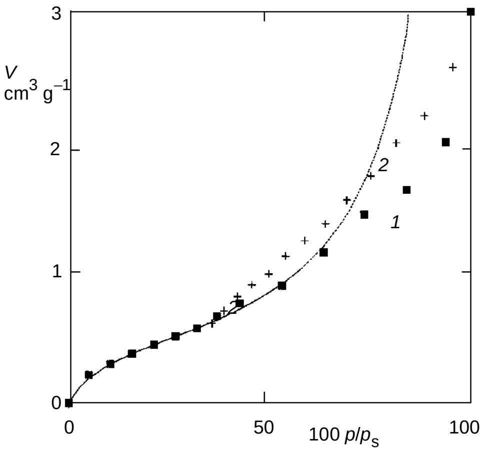

FIG. 2

Nitrogen adsorption isotherm at –196 °C for carbonizate HTT = 500 °C; experimental points: *1* adsorption branch, *2* desorption branch. Curve represents part of isotherm calculated from BET equation

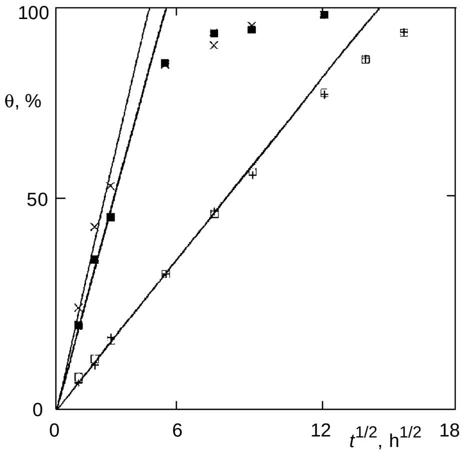

FIG. 3

Example of determination of diffusivity D_s from experimental data, case of wetting; θ is mean relative water concentration inside solid phase. ❐ HTT 400 °C, humidity 100%, + HTT 400 °C, humidity 44%, ■ HTT 600 °C, humidity 100%, × HTT 600 °C, humidity 44%

concentration of water θ inside the specimen (θ < 0.5) and for the case of a constant concentration c_s at the plate periphery, is known in the form[22]

$$\theta = \frac{m - m_0}{m_\infty - m_0} = \left[\frac{4 D_s t}{L^2 \pi} \right]^{1/2} , \qquad (4)$$

where L is half the plate thickness, m_0, m, and m_∞ are the specimen masses at time $t = 0$, t, and $t \to \infty$, respectively.

Diffusivity D_s was evaluated from the slope of dependence of θ vs $t^{1/2}$. All these dependences had, for θ < 0.5 in agreement with Eq. (*4*), a straight-line shape. The determination of diffusivity is illustrated in Fig. 3.

The dependences of D_s on HTT for the case of wetting and drying are plotted in Figs 4 and 5. The dependences correspond to the measurements of differently carbonized specimens at the relative humidity 100 and 44%. The diffusivities measured on drying (130 °C) are nearly hundred times greater than the corresponding diffusivities measured on wetting (20 °C). The dependences measured for the cases of 100 and 44% relative humidity are almost identical with the exception of values HTT 500 to 600 °C.

The shape of dependences of diffusivities on HTT is fairly similar for the case of wetting and drying. The diffusivities measured on drying and wetting are up to HTT = 350 °C nearly constant. At higher HTT, they at first mildly, then more strongly increase up to HTT = 600 °C when the dependence reaches its maximum. The diffusivities for glassy carbon (HTT = 750 up to 950 °C) are again low, however, higher than those for the case of resite. In comparison with the dependence of porosity on HTT, in this case the maximum is reached 150 °C sooner.

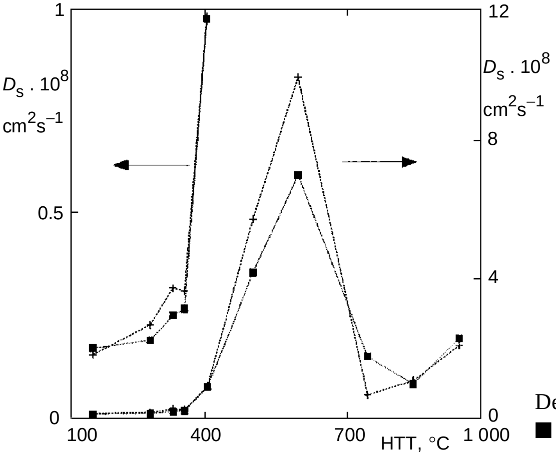

FIG. 4
Dependence of D_s on HTT, case of wetting: ■ humidity 100%, + humidity 44%

Mass Transfer in Carbonized Resite

On the basis of results of study of the porous structure development, it is possible to exclude the transport of gases through macropores, i.e., the bulk diffusion and viscous flow. In this study, two models will be considered which could describe transport of water vapour in specimens from resite carbonized to various temperatures.

Model of occluded gas[22,23] describes the gas diffusion in carbonizates from polymer precursors such as the gas would be dissolved (occluded) in the solid substance. This approach is generally used for the description of diffusion in polymeric substances[24] and in carbonaceous molecular sieves[22,23]. The driving force of mass transport is the concentration gradient $\mathrm{d}c_s/\mathrm{d}x$ in which the concentration c_s of diffusing component is related to volume unit of the solid phase (including the pores if any). The validity of the Fick laws with a constant diffusivity designated as D_s in the entire concentration range is assumed.

Model of gas diffusion in pores[22,23]. In this case it is assumed that the transport of molecules is realized in the gas phase, i.e., in the pore network. The driving force of mass transport is in this case the concentration gradient in the gas phase so that the first Fick law can be in this case written by the equation

$$N = -D_g \frac{\mathrm{d}c_g}{\mathrm{d}x} \quad , \tag{5}$$

where N is the molar flow related to the unit of cross section of porous medium (mol/cm^2 s), D_g is the diffusivity of the gas component in porous substance and c_g is the concentration of diffusing gas in the gas phase inside the porous structure, $c_g = p_i/\boldsymbol{R}T$, p_i being its partial pressure. The value of D_g corresponding to the temperature of 20 °C

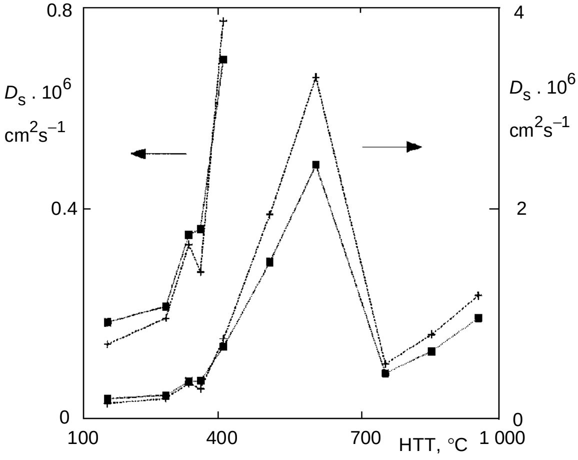

FIG. 5

Dependence of D_s on HTT, case of drying: ■ humidity 100%, + humidity 44%

can be calculated from the determined value of D_s on the basis of the relation which follows from the Fick law written in terms of D_s, c_s and D_g, c_g

$$D_g = D_s \frac{dc_s}{dc_g} \ . \tag{6}$$

The establishing of the adsorption equilibrium is assumed. Quantity dc_s/dc_g represents the slope of adsorption isotherm. This fact may be exploited under certain conditions for the identification of adequate model. If the isotherm is linear, $c_s = H\, c_g$, both the models may formally comply regardless of the actual mechanism for

$$D_g = HD_s \ , \tag{7}$$

where H is the Henry constant.

If the adsorption isotherm is curved then both these models may not comply – in case that one of them satisfies, the diffusivity of the second has to be concentration-dependent. The degree of curvature was judged on the basis of comparison of values of the Henry constant (formally defined as $H = c_s/c_g$) determined for the two studied levels

TABLE III
Water adsorption in carbonizates at 20 °C after reaching equilibrium at relative humidity 100 and 44%; *H* is Henry constant

HTT, °C	Adsorption, vol.%		10^{-3} *H*, cm_g^3/cm_s^3	
	100%	44%	100%	44%
150	5.20	2.81	3.00	3.68
275	6.19	3.31	3.57	4.35
325	7.21	3.44	4.16	4.52
350	7.12	3.33	4.11	4.37
400	6.27	3.05	3.62	4.00
500	5.58	1.80	3.10	2.36
600	9.65	1.85	5.57	2.43
750	14.55	8.62	8.40	11.31
850	10.08	5.42	5.82	7.12
950	3.43	2.06	1.98	2.71

of relative humidity, see Table III. These values were determined from the absorbed amount of water after establishing equilibrium on wetting.

In the region of HTT up to 400 °C, the corresponding pairs of *H* values do not differ very much so that the identification of adequate model is not possible. The corresponding pairs of D_s are, within the range of experimental error, close each other as well so that it is possible to state that both the models are formally satisfactory.

For HTT 500 and especially 600 °C, the curvature of adsorption isotherm occurs for the value of *H* for higher relative humidity has higher value (for 600 °C 2.3 times). In case of adequacy of the model of occluded gas, the corresponding pairs D_s should be identical. For the case of 100% relative humidity, however, lower values were found out (see Figs 4, 5). If the model of gas diffusion in pores held, i.e., D_g = const., then the diffusivity D_s should be concentration-dependent and take lower values for higher c_g (see Eq. (*6*)) in harmony with the found facts.

For the model of gas diffusion in pores, the diffusivity D_g should depend on porosity, tortuosity and pore size. With regard to the fact that the porous structure is formed mostly by micropores, we may consider the values calculated from the micropore volume for the porosity, see Table I. The dependences of D_g on HTT are plotted in Fig. 6 for both the levels of relative humidity, D_g values being determined from Eq. (*7*). The values of D_g begin to increase in the vicinity of HTT 400 °C analogously to the values $\varepsilon = w_0\rho_b$. The relative increase of values of D_g is, however, more expressive, which can be explained by increasing the pore orifices which is greatest for the temperature of 600 °C (the greatest nitrogen adsorption, see Table II). After surpassing this value, diffusivity decreases, which can be explained by diminishing the pore orifices whereas the micropore porosity still increases up to HTT 750 °C. The following decrease of micropore porosity is caused by closing the pores. For the increase of D_s values in the interval of

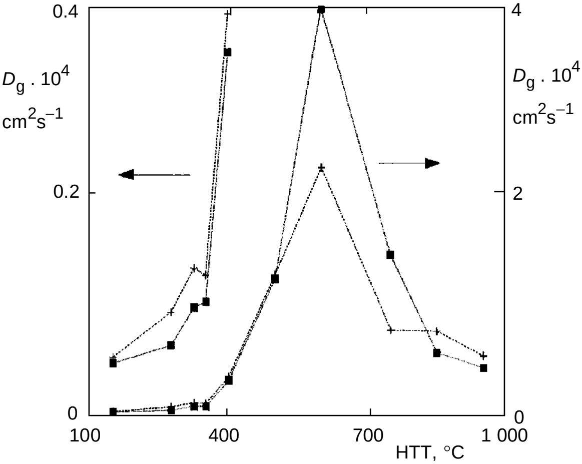

FIG. 6
Dependence of D_g on HTT, case of wetting: ■ humidity 100%, + humidity 44%

HTT 750 to 950 °C, the explation is missing, and therefore the model of gas diffusion seems more probable in this interval of HTT.

An analogous growth of the methane diffusivity in the vicinity of HTT = 400 °C, attainment of the maximum in the vicinity of 600 °C and subsequent decrease were also observed by Koresh and Soffer[6] in case of a thin-walled capillary membrane from further unspecified cross-linked polymer carbonized at various HTT. The hydrogen diffusivity had an analogous shape with this difference that the diffusivity decrease took place after surpassing HTT = 750 °C. These results are in agreement with the conception of gradual development and closing of micropores in the course of carbonization, the closing of orifices of these micropores manifesting itself in the value of diffusivity sooner in case of methane which consists of greater molecules. The high selectivity as for the hydrogen diffusion is typical of the gas separation on microporous membranes.

Dependence of Diffusivity on Temperature

The rate of gas transport in carbonized specimen depends partly on the transport properties of material which are connected with its structure being formed in the course of carbonization, partly on the temperature which influences the velocity of motion of molecules diffusing through this structure. The former was expressed by the dependence of diffusivities of carbonizates on HTT, the latter will be discussed in this part.

To express the dependence of diffusivity on temperature, the activated diffusion is usually assumed for polymers and microporous substances of the character of molecular sieves. This dependence for the model of occluded gas can be expressed as[22,23]

$$D_s = D_{s,0} \exp\,(-E/\boldsymbol{R}T)\ , \qquad (8)$$

where $D_{s,0}$ is the preexponential factor and E is the activation energy.

For the model of gas diffusion in pores, where the Arrhenius equation for coefficient D_g is considered, the dependence of diffusivity D_s on temperature is to be expressed with respect to Eq. (*7*) as[22,23]

$$D_s = (D_{g,0}/H_0) \exp\,[-(E - \Delta H^0)/\boldsymbol{R}T]\ , \qquad (9)$$

where ΔH^0 is the adsorption enthalpy (usually $\Delta H^0 < 0$). Therefore, it is apparent that the dependence of experimentally determined diffusivity D_s on temperature can be for both the models formally expressed by the same equation taking into account that in the second case, the apparent activation energy is concerned which is a sum of the true activation energy and heat of adsorption.

The activation energies were calculated from all the corresponding pairs of measurements (wetting 20 °C – drying 130 °C) at the same relative humidity. The resultant values are given in Table IV for various HTT. It is apparent that for the two levels of relative humidity, relatively close values of activation energy are obtained in agreement with expectation. The highest activation energies were found out for HTT up to 400 °C (average value 41 kJ/mol), in the region 500 to 600 °C, lower values (average 31 kJ/mol) were found out and for the region of HTT $\geq$ 750 °C, the average value 35 kJ/mol was determined.

For two values of HTT, 275 and 325 °C, an additional attempt was carried out of drying the samples at the temperature of 215 °C. The activation energies calculated from the triad of measuring temperatures (20, 130 and 215 °C), 41 and 44 kJ/mol were obtained for HTT 275 and 325 °C, which are values close to the values calculated from the pair of temperatures (20 and 130 °C). The parameters of Eq. (*8*) for carbonizates corresponding to various values of HTT evaluated from the measurement of wetting and drying at the two levels of relative humidity.

These parameters were used for estimating diffusivity under the conditions of carbonization, i.e., at temperature T. When extrapolating the diffusivity to the temperature of carbonization T in terms of Eq. (*8*), the parameters D_0 and E were used found out for a specimen carbonized to this temperature (T = HTT). The extrapolated values of D_s calculated in this way are illustrated in the Arrhenius diagram, Fig. 7. These points can

TABLE IV
Parameters of Eq. (*8*) for various carbonizates. Activation energies E were calculated from the two levels of relative humidity together and separately

HTT, °C	$10^3\ D_{0,s}$, cm^2/s	E, kJ/mol	E(100%)[a] kJ/mol	E(44%)[a] kJ/mol
150	33.7	40.98	41.74	40.21
275	40.4	40.82	42.10	39.55
325	123.1	42.83	44.06	41.59
350	90.6	42.03	43.80	40.26
400	72.0	38.51	38.06	38.95
500	21.9	31.62	31.82	31.41
600	34.0	31.41	31.57	31.25
750	10.0	33.10	28.18	38.03
850	51.0	37.33	36.77	37.90
950	31.2	34.40	33.07	35.73

[a] In parentheses are data on relative humidity.

be in the temperature interval 150 – 600 °C eligibly fitted to a straight line corresponding to an only pair of parameters $\overline{D}_0$ = 0.475 cm^2/s and $\overline{E}$ = 50.5 kJ/mol. The parameters averaged in this way may formally be used for estimating diffusivity at arbitrary temperature of carbonization in terms of Eq. (*8*). However, it is necessary to realize that all the given diffusivity estimates obtained by extrapolating are very rough and usable only for lower carbonization temperatures. For comparison also the points calculated for single levels of relative humidity are plotted in Fig. 7. It is evident that the extrapolated values calculated for relative humidities 100 or 44% do not practically differ.

From the analysis of the presented results of development of porous structure and measurements of diffusivities it is possible to formulate the following ideas of character of diffusion in differently carbonized resite: At HTT up to 350 to 400 °C, the carbonized specimen has the character of polymer substance with low diffusivity and high activation energy. In this region, the diffusion is to be well described by the model of occluded gas. With increasing HTT, the development of microporous system of the type of molecular sieves takes place. It is connected with a considerable increase in difusivity, decrease in activation energy and/or even change of diffusion mechanism (model of gas diffusion in pores). Starting from the temperature of 600 °C, the micropore orifices begin to diminish (decrease in diffusivity and increase in activation energy) whereas the micropore volume is still increasing up to 750 °C. After surpassing this temperature, the microporous system is gradually closed (decrease in open microporosity).

The proportion of mesopores, if any, of the gas transport in carbonized resite is difficult to judge for the information on their occurrence is available only for HTT 400 and 500 °C. Considering that their volume is multiply lower than that of micropores and with respect to the discussed relations between the microporous structure and transport properties, it is possible to judge that this proportion is not dominant.

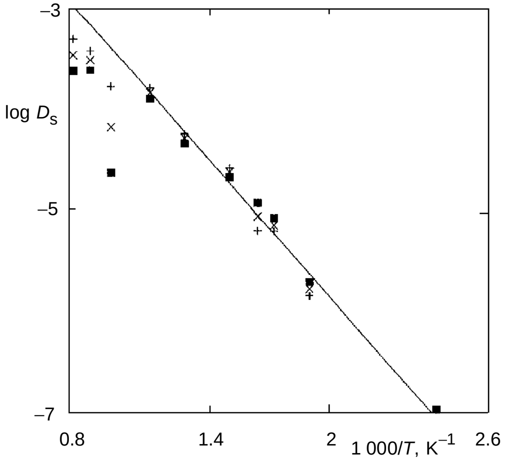

FIG. 7
Extrapolated dependence of diffusivity D_s (cm^2 s^{-1}) on temperature: ■ humidity 100%, + humidity 44%, × humidity (100 + 44%)

This research was supported by the Grant Agency of the Czech Republic, project No. 104/94/0596.

REFERENCES

1. Jenkins G. M., Kawamura K.: *Polymeric Carbons*. Cambridge University Press, Cambridge 1976.
2. Fitzer E., Shaefer W., Yamada S.: Carbon *7*, 643 (1969).
3. Fitzer E., Shaefer W.: Carbon *8*, 353 (1970).
4. Rautavuori J., Tormala P.: J. Mater. Sci., Lett. *14*, 2020 (1971).
5. Cowlard F. C., Lewis J. C.: J. Mater. Sci. *2*, 507 (1967).
6. Koresh J. E., Soffer A.: J. Chem. Soc., Faraday Trans. *82*, 2057 (1986).
7. Hatori H.: Carbon *30*, 719 (1992).
8. Lausevic Z., Marinkoviç S.: Carbon *24*, 575 (1986).
9. Yamashita Y., Ouchi K.: Carbon *19*, 89 (1981).
10. Glogar P., Balik K., Kolar F., Marek J.: Acta Montana, B *85*, 83 (1992).
11. Choe C. R., Lee K. H., Yoon B. L.: Carbon *30*, 247 (1992).
12. Kolar F., Fott P.: *Proceedings of the Xth International Symposium on Carbon and Graphite Materials, Raciborz 1993*, IV-17. Research and Experimental Production Center ZEW S.A., Raciborz 1993.
13. Siebeneck H. J.: Carbon *15*, 187 (1977).
14. Bunnel L. R.: Carbon *12*, 693 (1974).
15. Fott P., Kolar F., Weishauptova Z.: Acta Montana, B *91*, 5 (1994).
16. McEnaney B., Mays T. J. in: *Introduction to Carbon Science* (H. Marsh, Ed.). Butterwords, London 1989.
17. Medek J.: Fuel *56*, 131 (1977).
18. Mahajan O. P., Walker P. L. in: *Analytical Methods of Coal and Coal Products* (C. Karr, Ed.), Vol. I, p. 125. Academic Press, New York 1978.
19. Moreno-Castilla C., Mahajan O. P., Walker P. L.: Carbon *18*, 271 (1980).
20. Walker P. L., Oya A., Mahajan O. P.: Carbon *18*, 377 (1980).
21. Barret E. P., Jonyer L. G., Halenda P. P.: J. Am. Chem. Soc. *73*, 373 (1951).
22. Walker P. L., Mahajan O. P. in: *Analytical Methods of Coal and Coal Products* (C. Karr, Ed.), Vol. I, p. 163. Academic Press, New York 1978.
23. Walker P. L., Austin L. G., Nandi S. P. in: *Chemistry and Physics of Carbon* (P. L. Walker, Ed.), Vol. 2. Dekker, New York 1966.
24. Meissner B., Zilvar Z.: *Fyzika polymeru*. SNTL, Praha 1987.