

# POSTER

## THE RELATIONSHIP BETWEEN THE MICROPOROSITY OF COKES AND THEIR RESISTANCE AND CARBOXYREACTIVITY

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### INTRODUCTION

A large number of coke properties depend on coke porosity. The technological properties of lump cokes are influenced by meso- and macropores originated from the discontinuous distribution of coke matter within the coke body. The physical properties of coke matter forming the rigid skeleton of coke are affected by the microporosity defined as a system of cavities of molecular size permeating the carbon solid phase. In the solid phase of coke matter there are concentrated all material properties whose quantities can be determined by their extrapolation to zero value of microporosity. As it is very difficult to prepare an individual carbon substance with graduated microporosity, it seems more practical to employ substances with very similar properties of the solid phase, but with different volume of micropores.

The above-mentioned alternative method is based on results published by OUCHI [1], who has found that carbonization products of various substances (bituminous coal, lignites, cellulose) exhibit, after pyrolysis above 500°C, only small differences of electrical conductivity. This could imply that aromatic nuclei acquire, by heat treatment, a very similar inner structure. Although such an assumption cannot be entirely generalized, it may be expected that the solid phase of cokes prepared under approximately the same conditions will have very similar physical properties.

The aim of this study was to investigate the microporosity effect on two important properties of metallurgical cokes - electrical conductivity and carboxyreactivity - and to derive, according to the correlation between textural parameters and these properties, their limit values for the coke solid phase.

### EXPERIMENTAL

The sample collection consisted of industrial metallurgical cokes from Ostrava-Karviná coking plants. The coke samples differed by content of individual coal components in the coke charge, final carbonization temperature and degree of maturation.

Volume of micropores  $V_{\text{micro}}$  was identified with limit sorption space  $w_0$  according to the  $\text{CO}_2$  isotherm at 25 °C. Surface area  $S_{\text{micro}}$  was computed by means of an independent method [2]. Resistivity  $\rho$  of the microporous coke matter was determined by a method published recently [3]. The method makes it possible to calculate the resistivity at arbitrary bulk density of the tested material. The resistivity values used in the present work were related to the density of the microporous coke matter. The carboxyreactivity was determined by the international standard method [4] in a flow reactor and expressed by effective reaction rate constant  $k_{\text{ef}}$ .

### RESULTS

Fig.1 shows the dependence of resistivity on volume  $V_{\text{micro}}$ , which is, in this case, the determining parameter, because the void volume of micropores creating the spatial discontinuity of the solid phase reduces the operative cross section of conductor. The shown linear relationship can be expressed by the equation

$$\rho = 0.0038 + 0.4405 V_{\text{micro}} \quad [\Omega\text{cm}].$$

For the mean resistivity of the non-porous solid phase of metallurgical cokes it follows  $\rho = 0.0038 \Omega\text{cm}$  with correlation coefficient  $r = 0.992$ .

Fig.2 shows the dependence of rate constant  $k_{\text{ef}}$  on micropore surface area  $S_{\text{micro}}$ . This quantity, as a microporosity parameter, corresponds better with the physical meaning of the reaction  $\text{CO}_2 + \text{C} = 2\text{CO}$ .

$$\frac{S_{\text{micro}}}{k_{\text{ef}}} = \frac{1}{k_{\text{ef(max)}} \cdot C} + \frac{S_{\text{micro}}(C+1)}{k_{\text{ef(max)}} \cdot C}$$

For the rectification of the relationship shown in Fig.2 the above-mentioned equation was used, where  $k_{\text{ef(max)}} = 2.12 \text{ cm}^3/\text{g/s}$  is the rate constant of conversion at maximum dispersion of the solid phase and the experimental points conform to linear form (Fig.3) with correlation coefficient  $r = 0.987$ .

## DISCUSSION

The direct proportionality of two different properties of carbon material to the microporosity enables to be drawn the following important conclusions.

First, the microporosity extent indicates that this part of the porous system must have its own physical sense that specifically modifies the inner structure of carbon matter.

If carbon matter is considered a dispersion system in which the solid phase is the continuous dispersion portion, the microporosity can then be interpreted as the dispersion degree of the solid phase.

Second,  $S_{\text{micro}}$ , which is a function of  $V_{\text{micro}}$ , will be the best convenient measure of the dispersion degree. Such a way of expressing microporosity also agrees with some ideas on its spatial arrangement [5]. The minimum dispersion will occur if the solid phase takes the minimum surface area. On the contrary, the maximum dispersion would occur if the solid phase spread out into a configuration with the maximum surface.

As an example of expressing the dispersion degree, the limit configurations of the graphite solid phase may be given. The unit mass of graphite (1 g) with density  $d_r = 2.25 \text{ cm}^3/\text{g}$  will have, in the form of a compact sphere, the minimum surface area  $S = 2.82 \times 10^4 \text{ m}^2/\text{g}$ . The degree of maximum dispersion of the unit graphite mass may be idealized by means of a single elementary lamella. The lamella - irrespective of the spatial arrangement - is confined, from both sides, by the total surface area  $S = 2840 \text{ m}^2/\text{g}$ . This area is by the order of  $10^7$  larger than that for the minimum dispersion. For cokes, the minimum and maximum surface areas of micropores were determined as  $4.72 \text{ m}^2/\text{g}$  and  $267 \text{ m}^2/\text{g}$ , resp. At the same time these values characterize the lowest and highest dispersion degrees of the solid phase of the metallurgical cokes under study.

## REFERENCES

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4. Method of measuring the reactivity of metallurgical cokes ST ECE Coal/12, N.Y., 1965
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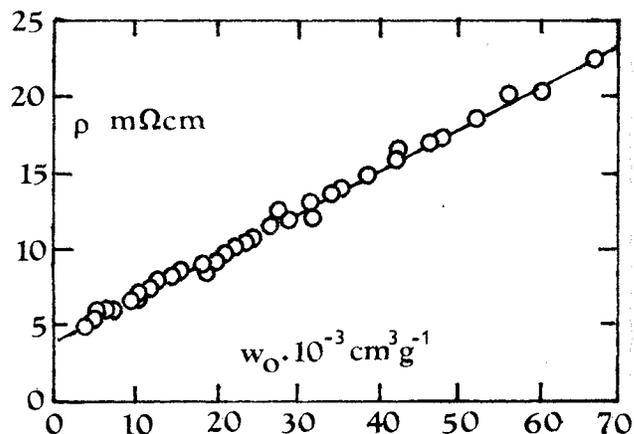


Fig.1. Dependence of coke resistivity  $\rho$  on micropore volume  $V_{\text{micro}}$

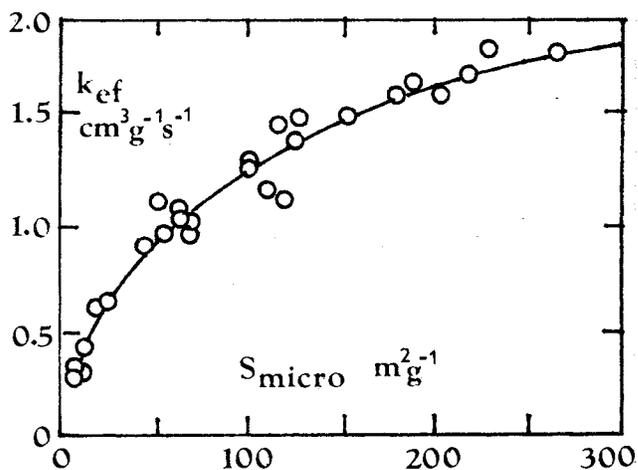


Fig.2. Dependence of coke reactivity on micropore surface area

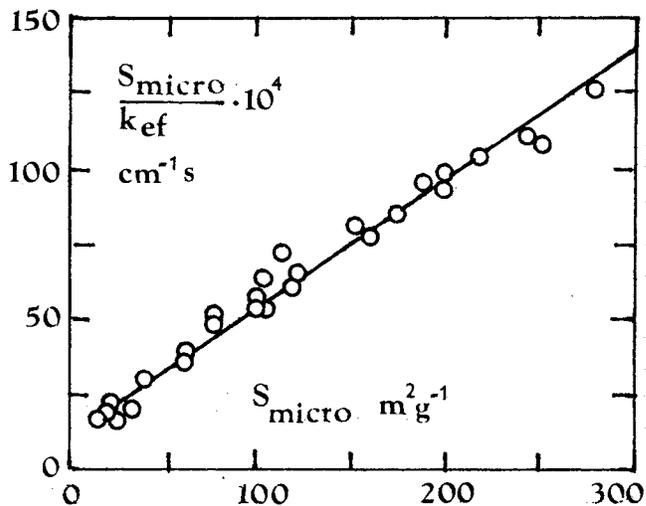


Fig.3. Linear relationship  $k_{\text{ef}}$  versus  $S_{\text{micro}}$