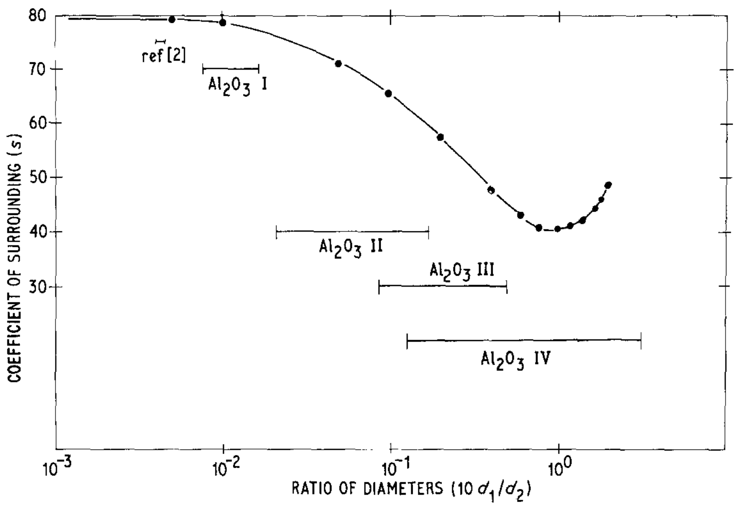

Figure 8 Evolution of the "coefficient of surrounding" against the ratio of sphere diameters.

alumina Al_2O_3 (IV) is in fact a mixture of non-reactive and reactive agglomerates, all shapes which are very different from spheres, the concept of the "coefficient of surrounding" enables us to separate the different kinetic behaviours. Above, the $d_1/d_2 \simeq 2 \times 10^{-2}$ geometrical factors appeared to be more and more important and models of kinetic powder reaction should take them into account. It is quoted in the introduction that in ceramics, as in other materials science fields, solid-state reactions are usually carried out by using fine powders in order to profit from their higher reactivity. Examination of the above results also shows that care must be taken in using fine powders of similar grain size in which reaction rapidly concentrates the product formed on portions of the host grain leading to difficulties in obtaining complete reaction.

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A comparative study of the electrical resistivities of different finely divided carbon materials under compression

The influence of the nature of the filler and binder, the two main raw materials used in the manufacture of carbon products, on the characteristics of the latter is well established in the literature [1–4]. In particular, the filler is of paramount importance since it constitutes about 85% of the final carbon and graphite. For example, in a recent study [5] to determine the effect of the nature of the filler materials on the physical

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characteristics of baked carbon mixes, the anthracite coal was found to give a baked carbon of significantly higher electrical resistivity and mechanical strength than calcined petroleum coke. A similar trend was also observed in the case of metallurgical coke. Further, the differences in the electrical resistivities of the product obtained using anthracite coal or metallurgical coke and the product obtained using calcined petroleum coke may not be compensated for completely by the selection of a better binder pitch or by a change in the processing conditions or both. Thus, while formulating the filler composition for a particular carbon product one has to have the knowledge of the relative characteristics of different carbon materials. In particular, for the electrical applications, one should consider the electrical resistivities of various filler materials which may be studied in terms of the electrical resistivities of their powders under compression. Also, the electrical resistivity of the coke powder is an important parameter in designing electrical furnaces for graphitization (e.g. Acheson furnace) since the temperature characteristics of the furnace depend largely upon the electrical resistance of the packing coke powder. Moreover, such a study may be useful in identifying different carbon materials and may give indications of their graphitizability. This is apparent from studies carried out by a number of workers [6–11]. Good authoritative studies of the electrical resistivities of carbon powders (namely certain petroleum cokes and carbon blacks) under compression have been carried out by Mrozowski [12–14]. However no such study on the different cokes or coals in the raw and calcined state seems so far to have been reported in the literature. In view of this, an attempt was made to study the electrical resistivities of finely divided petroleum coke, pitch coke, metallurgical coke and anthracite coal in raw and calcined states, under compression. The present communication is the result of this investigation.

TABLE I Characteristics of the different carbon materials

Material	Ash content (%)	Volatile matter content (%)	Kerosene density (g cm^{-3})
Petroleum coke	0.96	Nil	2.10
Pitch coke	1.76	1.54	1.89 1.93*
Metallurgical coke	6.26	2.9	1.97 1.97*
Anthracite coal	12.89	8.0	1.83 1.93*

*Refers to the calcined material.

The different carbon materials used in the present study, namely, petroleum coke, pitch coke, metallurgical coke and anthracite coal are characterized in Table I. They were crushed, ground and then partly sieved to obtain different sized fractions. Except the petroleum coke which was already calcined, the remaining unsieved parts of the different materials were calcined in an inert atmosphere to a temperature of 1150° C for 1 h in order to remove their volatile components. These calcined materials were then sieved to obtain different sized fractions as above. Thus, powders of specific sizes of the different carbon materials both in the raw and calcined states were obtained. The various carbon powders were finally subjected to electrical resistivity measurements. The experimental instruments for these measurements consisted of a sample holder, a 5 tonne capacity electrically operated compression machine, a 30 V, 10 A d.c. power supply, a precision ammeter and a solid-state d.c. microvoltmeter. The sample holder consisted of a vertical thick-walled perspex cylinder of length 14 cm and internal diameter 20 mm resting on a thick brass plate, into which a thick brass plate piston moved freely. Prior to the electrical resistivity measurements, the carbon powders were heated in an oven at a temperature of 110° C for 1 h and then cooled in a desiccator to remove any moisture. The moisture-free carbon powders were poured into the cylinder and compressed by means of the piston, using the compression machine, to pressures ranging from about 30 to 220 kg cm^{-2} in a series of steps. Except for raw anthracite coal, for which a current of 2 mA was used, a current of 0.2 A was passed through the powder bed and the potential drop across it was measured using the microvoltmeter. The height of the powder column was measured to an accuracy of 0.01 cm. From these observations, the electrical resistivity was calculated using Ohm's law. Care was taken to see that no powder was wedged between the walls of the cylinder and the piston, since this may otherwise

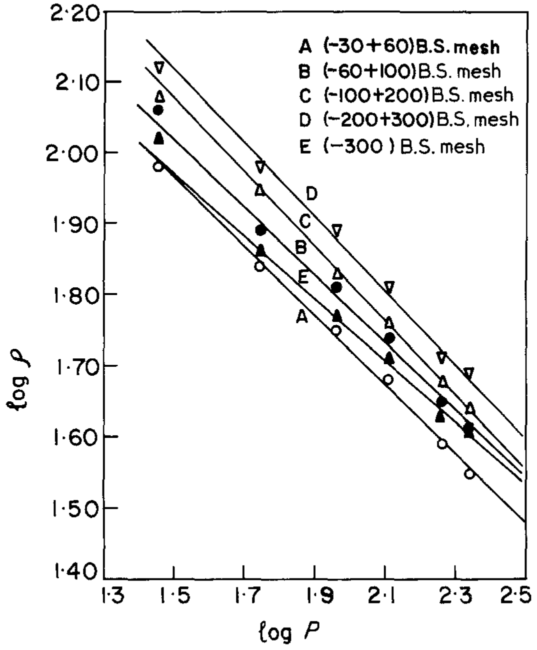

Figure 1 Log ρ against log P plot for calcined pitch coke of different sizes.

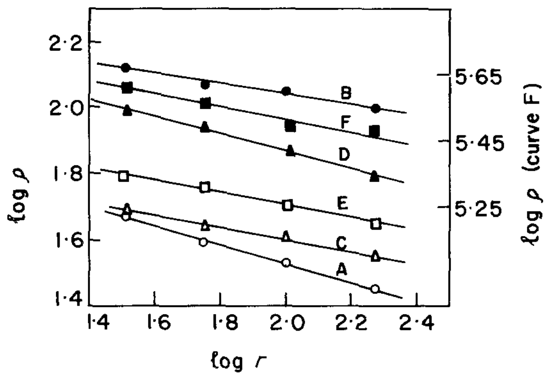

Figure 2 Log ρ against log r plot for calcined petroleum coke (A), raw pitch coke (B), calcined pitch coke (C), raw metallurgical coke (D), calcined metallurgical coke (E) and raw anthracite coal (F).

reduce the pressure applied on the powder and thus invalidate the results.

Fig. 1 shows the pressure dependence of electrical resistivity curves for a typical carbon material, namely, calcined pitch coke in different sizes. Fig. 2 represents the electrical resistivities of the different carbon materials measured at the highest pressure (220 kg cm^{-2}), as a function of particle size on a log–log scale. The results of the electrical resistivity measurements of these materials, in raw and calcined forms, fractionated into different sizes using British Standard (BS) test sieves, at the highest pressure of measurement, are given in Table II along with the slopes of the pressure dependence of the resistivity curves. The packing densities in each of the above cases are listed in Table III. The ratios of the electrical resistivities of the calcined materials for different sizes are given in Table IV. The slopes of the size

TABLE II Electrical resistivities of different carbon materials in different sizes in raw and calcined states

Material	State	Electrical resistivities (m ohm cm) measured for various BS mesh sizes*				
		(− 30 + 60)	(− 60 + 100)	(− 100 + 200)	(− 200 + 300)	(− 300)
Petroleum coke	Raw	–	–	–	–	–
	Calcined	28.4 (0.53)†	34.2 (0.58)	38.6 (0.53)	46.3 (0.51)	41.7 (0.47)
Pitch coke	Raw	99.6 (0.71)	112.7 (0.66)	117.6 (0.60)	132.9 (0.64)	135.5 (0.64)
	Calcined	35.1 (0.48)	40.5 (0.47)	44.1 (0.52)	49.1 (0.52)	40.3 (0.44)
Metallurgical coke	Raw	61.3 (0.58)	73.4 (0.56)	87.9 (0.59)	97.3 (0.61)	84.1 (0.55)
	Calcined	44.4 (0.48)	50.8 (0.50)	57.0 (0.50)	62.1 (0.50)	42.6 (0.43)
Anthracite coal	Raw	305×10^3 (0.60)	308×10^3 (0.60)	360×10^3 (0.55)	404×10^3 (0.54)	397×10^3 (0.51)
	Calcined	197.3 (0.54)	157.8 (0.54)	163.2 (0.54)	263.0 (0.50)	175.6 (0.56)

*Measurements taken at a pressure of 220 kg cm^{-2}.

†The figures in parentheses denote the slopes of the log ρ against log P curves.

TABLE III Packing densities of different carbon materials in different sizes in raw and calcined states

Material	State	Packing densities (g cm^{-3}) measured for various BS mesh sizes*				
		(– 30 + 60)	(– 60 + 100)	(– 100 + 200)	(– 200 + 300)	(– 300)
Petroleum	Raw	–	–	–	–	–
coke	Calcined	1.26	1.24	1.27	1.24	1.42
Pitch	Raw	1.09	1.09	1.14	1.07	1.39
coke	Calcined	1.13	1.17	1.18	1.16	1.39
Metallurgical	Raw	1.17	1.13	1.11	1.09	1.44
coke	Calcined	1.13	1.12	1.13	1.11	1.44
Anthracite	Raw	1.24	1.12	1.13	1.10	1.31
coal	Calcined	1.04	0.97	0.96	0.98	1.31

*Measurements taken at a pressure of 220 kg cm^{-2}.

dependence of electrical resistivity curves on a log–log scale for the different materials are given in Table V.

It may be mentioned here that the variation of electrical resistivity with pressure on a log–log scale yields a straight line regardless of the type and size of the carbon material. However, the slopes of these straight lines vary within a narrow range as seen in Table II. This is in very good agreement with the relation $\rho \cong P^{-1/2}$ observed by Mrozowski [12–14] for certain petroleum cokes and carbon blacks where ρ is the electrical resistivity and P is the applied pressure. It may also be noted that the slopes of the pressure dependence of resistivity curves are higher for a particular carbon material in the raw state than in the calcined state. This may be attributed to the oxide film either already present or formed on the surface of particles of the raw carbon material during the size reduction operation, as noticed by Mrozowski [12–14].

The calcination of the different carbon materials, namely, pitch coke, metallurgical coke and anthracite coal, results in a fall in their electrical resistivity. As may be clearly seen from Tables I and II, the electrical resistivity of the pitch coke (volatile matter (VM) = 1.54%) decreases by an average of 65%, that of metallurgical coke (VM = 2.80%) by an average of 35% and that of anthracite coal (VM = 8.0%) by more than three orders of magnitude. This is because of the escape of the volatile matter during calcination, in the form of hydrocarbons and hydrogen from the peripheries of the condensed ring systems in the raw carbon materials [15]. It may be noted here that although the proportion of volatile matter in the metallurgical coke is higher than that in the pitch coke, the fall in the electrical resistivity is higher in the latter case. This may be attributed to the inherent differences in the structure of the two materials. Thus, the degree of fall in the electrical resistivity of a raw carbon material as a result of calcination, appears to be related to its structure as well as to the volatile matter content.

Table II gives the electrical resistivities at a pressure of 220 kg cm^{-2}, for the different carbon materials, in raw and calcined states, fractionated into different sizes using BS test sieves. It can be seen that for any raw or calcined carbon material, the electrical resistivity increased as the particle

TABLE IV Ratios of the electrical resistivities of different calcined carbon materials as a function of size of the material

BS mesh size	Electrical resistivities (on an arbitrary scale) of the material			
	Calcined petroleum coke	Calcined pitch coke	Calcined metallurgical coke	Calcined anthracite coal
(– 30 + 60)	1	1.24	1.56	6.95
(– 60 + 100)	1	1.18	1.49	4.61
(– 100 + 200)	1	1.14	1.48	4.23
(– 200 + 300)	1	1.06	1.34	5.68
(– 30)	1	0.97	1.02	4.21

TABLE V Slopes of the electrical resistivity against particle size (radius) curves drawn on a log–log scale

Material	Slope
Calcined petroleum coke	-0.29
Raw pitch coke	-0.16
Calcined pitch coke	-0.18
Raw metallurgical coke	-0.26
Calcined metallurgical coke	-0.19
Raw anthracite coal	-0.20

size of the material decreased to (− 200 + 300) BS mesh. However, for the (− 300) BS mesh fraction, it decreased significantly compared to that of the (− 200 + 300) fraction. The increase in resistivity with decrease in particle size to (− 200 + 300) BS mesh cannot be accounted for by the packing density which varies only marginally, as shown in Table III. In fact a similar observation was made by Mrozowski [12] who termed it as the "size effect". According to him, this effect is very general but its nature is not clear. The decrease in the resistivity of the (− 300) BS mesh fraction in spite of the "size effect", on the other hand, may be attributed to the significant increase in the packing density of the material, over that of the (− 200 + 300) BS mesh fraction. This is due to the occupation of interparticle spaces formed by the packing of bigger particles by the relatively smaller particles. This results finally in an overall increase in the area of contact of the particles.

Quantitatively, a plot of the electrical resistivity of the different sized fractions of any carbon material against the average particle size (radius), yields a straight line with a negative slope on a log–log scale, as plotted in Fig. 2. However, the slopes obtained in the different cases vary from − 0.16 to − 0.29 as listed in Table V. This is in very good agreement with the relation $\rho \cong r^{-1/4}$ (r denotes the average size (radius) of the particles) observed by Mrozowski [12, 13] for some petroleum cokes and carbon blacks.

A comparison of the electrical resistivities of petroleum coke (PC), pitch coke (P′C), metallurgical coke (MC) and anthracite coal (AC), all in the same state of calcination, reveals that for the different materials with a given size,

$$(\rho)_{\mathrm{PC}} < (\rho)_{\mathrm{P'C}} < (\rho)_{\mathrm{MC}} \ll (\rho)_{\mathrm{AC}}. \qquad (1)$$

This may be attributed to their structural differences. However as given in Table IV, the relative degree of inequality among the electrical resistivities of the above materials, in general, decreases as the particle size of the materials decreases.

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