THE SHAPE OF GROUND PETROLEUM COKE PARTICLES

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The projected area per gram, envelope volume per gram and number of particles per gram have been measured for a number of sized coke fractions, in the range from 70 to 600 microns. The coke fractions were derived from two lump cokes of different origin and were prepared by sieving after crushing and grinding in five different combinations of industrial equipment. Shape factors, defined as the ratio of two diameters based respectively on the mean projected area and mean envelope volume of the individual coke particles, have been calculated from the measurements. For one coke the variations of shape with size was found to be substantially independent of the means of grinding; for the other significant variations between different types of grinder were obtained. An attempt has been made to interpret the results semi-quantitatively in terms of the pore and fissure structure of the original coke. The possible significance of the results to graphite manufacture is discussed.

Part I. Factors Affecting Particle Shape

Introduction

Artificial graphite bodies are normally prepared from a mixture of ground petroleum coke and a semi-liquid binder, the mixture being formed to the required shape by moulding or extrusion. Since the coke particles are irregular in shape they are oriented in the forming process and the presence of such oriented particles may be demonstrated, even in the finished graphite, by examination of polished sections at low magnification[1].

Petroleum cokes are known to be microcrystalline, with crystallites of about 20 Å linear dimension, and the *c* axes of these crystallites generally show a small preferential ordering in the direction of the shorter dimension of the particles. The particle orientation in the forming process therefore leads, in the finished graphite, to the preferred crystallite orientation which is evident in X-ray reflection photographs. The crystallite orientation is responsible for the anisotropy of such physical properties as electrical resistivity, thermal conductivity and coefficient of thermal expansion. It follows that this anisotropy should be affected by the shapes of the petroleum coke particles. Part I of this paper reports measurements of the effect on shape of particle size, type of coke and type of size reduction equipment.

Experimental

A. *Preparation of Samples*

In a typical series of experiments the selected coke, in the form of lumps 3–4 inches in size, was broken down in the selected equipment and the final product split, by sieving, into closely sized fractions. The sieves used were normally the Nos. 16, 22, 36, 52, 72, 100, 120, 200 and 240 British Standard Test Sieves (B.S. Spec. 410–1942).

For all grindings, conditions were arranged to give a final product which all passed a No. 22 B.S. sieve and of which approximately 60 per cent passed a No. 60 B.S. sieve. The only single stage grinder used was a Swing Sledge Mill. The other grind-

[1] J. M. Hutcheon, J. Inst. Fuel **26**, 309 (1953).

TABLE I
Densities of Cokes

Coke	A	B
Lump density (g/cc)	1.0–1.2	0.6–1.6
Real density (g/cc)	1.93	1.95

ings were done in two stages, a Rotary Fine Crusher being used to give a product of about $\frac{1}{4}$ inch size, which was then fed to the second stage. These machines are briefly described below.

Swing Sledge Mill (I)

This is a disintegrator in which arms with freely swinging hammers at their ends rotate at high speed (2000 r.p.m.) in a vertical plane. The material to be crushed is fed between vertical plates through the space traversed by the arms and hammers and passes out through a $\frac{1}{8}''$ grate.

Rotary Fine Crusher/Sample Grinder (II)

The rotary fine crusher has a fluted, approximately conical beater which rotates, at 125 r.p.m., on a vertical axis within a fluted casing. The Sample Grinder is a laboratory piece of equipment in which the material passes between two vertical hardened steel plates, one of which is fixed while the other rotates, at 750 r.p.m. on a horizontal axis.

Rotary Fine Crusher/Steel Rod Mill (III)

The latter is a rod mill of standard pattern, the mill casing being 10 inches in diameter and 12 inches long. The speed was 60 r.p.m. for Coke A and 28 r.p.m. for Coke B.

Rotary Fine Crusher/Crushing Rolls (IV)

The rolls are 8 inches in diameter by 5 inches long and rotate at 360 r.p.m.

Rotary Fine Crusher/Laboratory Disintegrator (V)

The latter is similar to the Swing Sledge Mill except that it is smaller, has no swinging hammers at the ends of the arms, and rotates at higher speed (7500 r.p.m.). For Coke A an 0.05 inch grate was used, but for Coke B the grate spacing was 0.035 inch.

B. *Types of Coke*

Two petroleum cokes were chosen. The first (Coke A) had uniform, relatively small pores and thick cell walls free from obvious fissures. The other (Coke B) was strongly fissured with widely varying pore size and cell wall thickness. Both cokes had previously been calcined at about 1300°C.

The lump densities and real densities (measured after refluxing in methanol) are shown in Table I.

Measurements and Definitions

An average particle shape constant, σ, for a group of particles has been defined by

$$\sigma = \frac{1.1 V^{\frac{1}{2}} N^{\frac{1}{2}}}{A^{\frac{1}{2}}} \quad \ldots\ldots\ldots \quad (1)$$

where V (cm^3/g) is the specific particle volume, A (cm^2/g) is the specific projected area and N is the number of particles per gram. These quantities were measured by methods previously described[2].

Wall thickness measurements were obtained from photomicrographs of plane polished sections of the coke lumps by a method analogous to that used in obtaining Martin's diameter in the microscopic measurement of particles. An arbitrary straight line was drawn across the photograph and the intercepts between adjacent pores were measured.

RESULTS

The shape constant was determined for each fraction and graphs constructed showing the variation of σ with mean particle size for each coke and each type of grinder. These graphs are shown in Figs. 1 and 2.

Since 180 experimental determinations

[2] T. Beirne and J. M. Hutcheon, Brit. J. App. Phys. Supp. No. 3, 576 (1954).

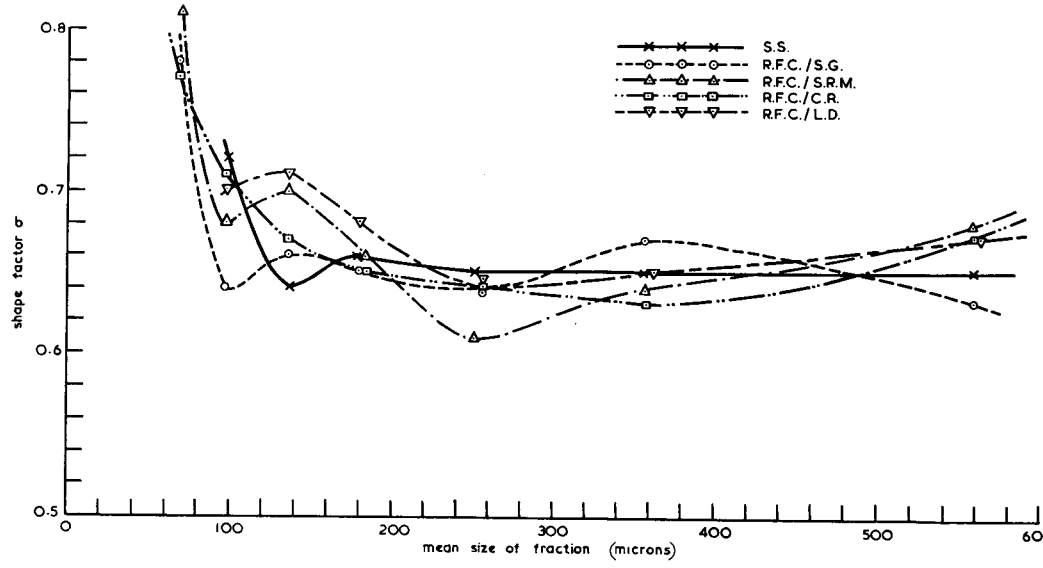


FIG. 1. Shape factor vs size for coke "A"

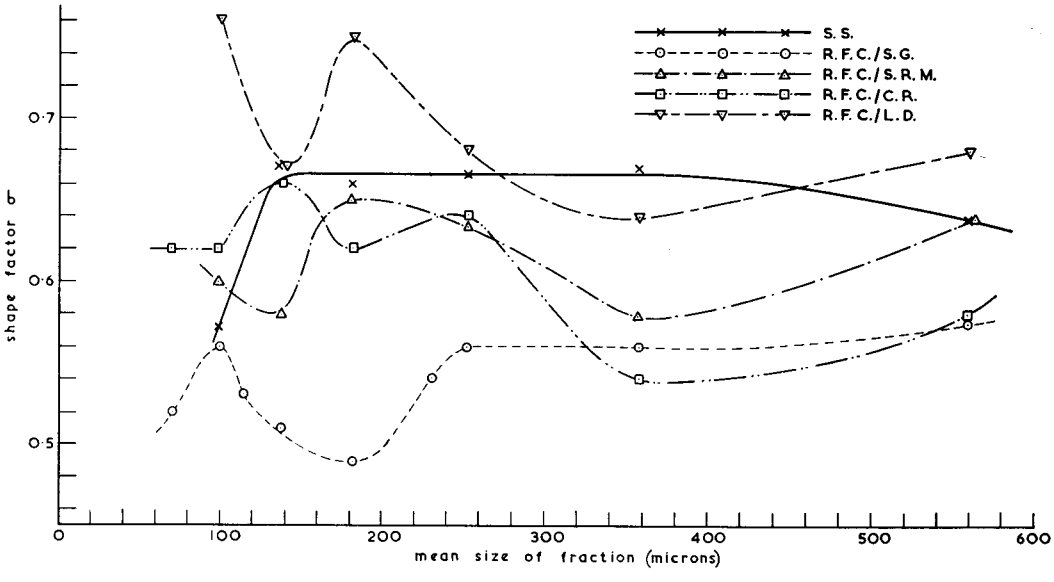


FIG. 2. Shape factor vs size for coke "B"

were required to obtain the shape constant data presented, the detailed experimental results are not quoted here.

The wall thickness measurements are shown as histograms for both types of coke in Fig. 3.

DISCUSSION

A. *General Concepts*

The curves shown in Figs. 1 and 2 are complex and any interpretation must involve several factors.

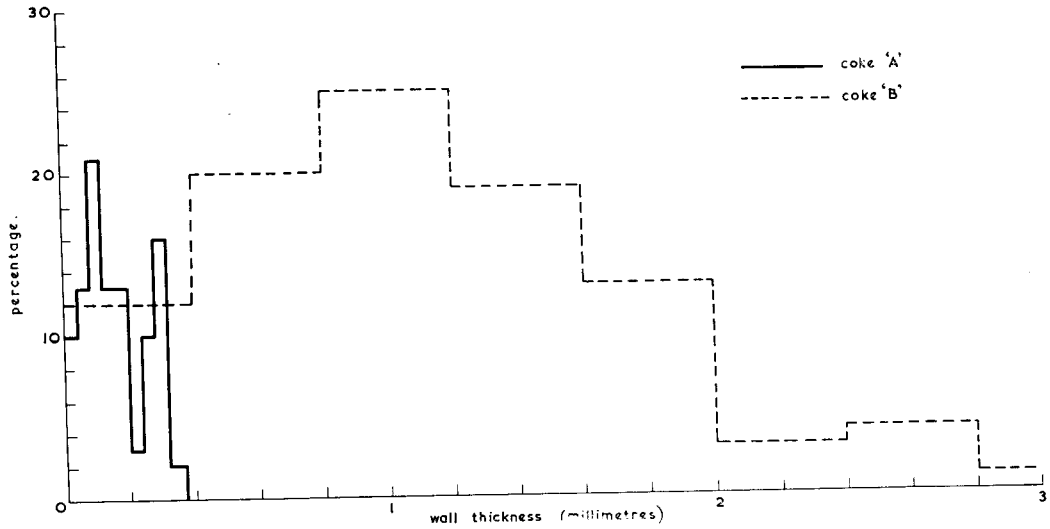


FIG. 3. Histogram showing frequency distribution of wall thickness within a coke lump

Two properties of the coke seem particularly important. These are firstly, fissures and secondly, cell-walls between pores. The fissures probably derive from shrinkage during coking as with coal cokes[3], while the pores are produced by the volatiles evolved. Evidence of both fissures and pores may be seen in the photomicrograph of a polished section of a coke lump given in Fig. 4.

The grinders used were of widely varying type. Again two features may be selected as the basis of a simplified analysis. One is the amount of energy delivered per impact by the machine on each particle; this may approximately be associated with the speed of the grinder. The second factor is the amount of recirculation taking place. Among the grinders studied this will be least with the crushing rolls and most with the steel rod mill.

B. *Interpretation of Curves for Coke A*

These concepts give some help to the interpretation of the observed curves. The simplest is given by Coke A in Grinder IV. (Fig. 1). For the coarser particles

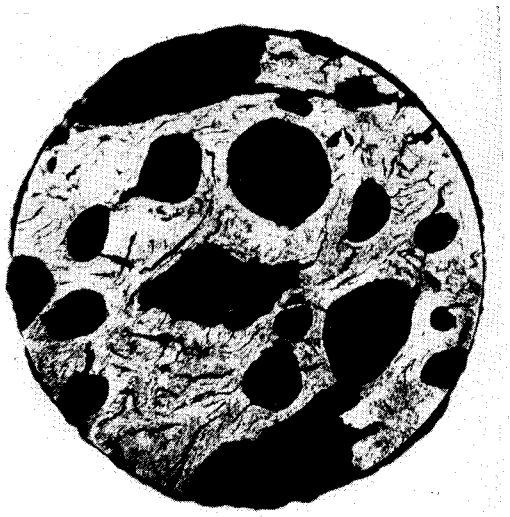


FIG. 4. Photomicrograph of polished section of coke lump, showing pores and fissures (× 46).

(600 μ) fracture is considered to take place preferentially along fissures i.e. by "cleavage". The shape factor therefore falls. For finer particles, however, this process gives way to fracture across the planes with a consequent increase in shape factor. The change may be because a minimum separation between fissures is reached, or because the flakes have become so thin that they are

[3] J. L. Soule, Fuel **34**, 68 (1955).

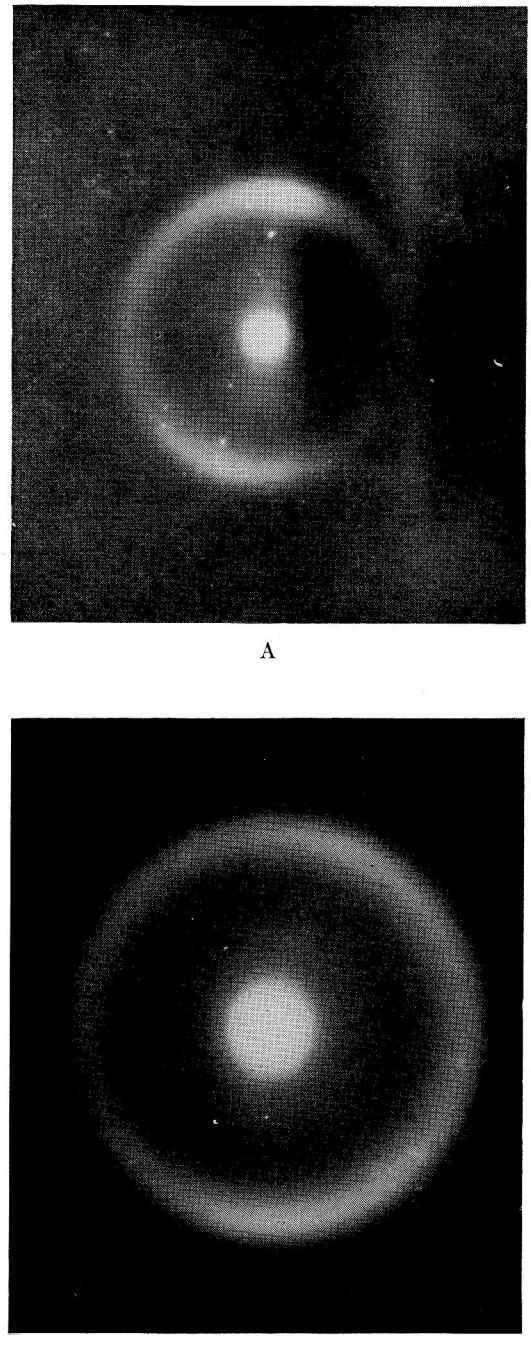
weaker across the planes than parallel to them. Apart from relatively minor features, the patterns for the other grinders are similar. For this coke therefore it appears that the anisotropic fissure structure of the coke exerts a predominant effect on the shape-size curve and the type of grinder used is of small consequence.

The almost constant shape factor shown by Grinder I from 600 μ down to 250 μ is of interest, however, especially as this behaviour is even more marked with Coke B. Also Grinder II shows a slight initial rise in this range and with Grinder V the fall is only slight. These grinders all operate at high speed. Bond[4] has shown that with low energy deposition, coal cokes fracture along fissures but that at high breaking energies, size reduction is by a different process and the cokes shatter into fragments of more or less random shape. Possibly the suppression by these high speed machines of the normal characteristics of fracture along fissures may be a similar phenomenon.

C. *Interpretation of Curves for Coke B*

For Coke B, the shape factor-size curves (Fig. 2) show more complex patterns individually and differ widely among each other. These differences are paralleled by differences in cell wall structure between the two cokes. For Coke A the majority of the cell walls are thicker than the coarsest particles examined, but for Coke B the entire distribution of cell wall thicknesses lies within the size range of interest (Fig. 3). Grinding eliminates the pores in the original coke lumps and releases these cell walls which, because of their thinness relative to the pore diameters (c.f. Fig. 4) are particularly flaky. (It is of interest that this material is also unusually highly oriented in the crystallographic sense, as is seen from the X-ray transmission photographs shown in Figs. 5a and 5b. The former was obtained by focussing the X-ray beam on a zone, 0.1

[4] R. L. Bond, Fuel **33**, 250 (1954).



A

B

FIG. 5. X-ray orientation photographs of "neck" between pores in lump of calcined coke A. A. X-ray beam focused on zone 0.1 mm. in diameter. B. X-ray beam oscillating over distance of 1 cm.

mm. in diameter, on the narrow neck between two pores. The latter was obtained with a beam which oscillated over a distance of 1 cm. on the coke lump.) The presence of these particles therefore superposes a second shape factor distribution on that arising from fissures present in the coke.

When this coke is ground in Grinder IV, the σ value diminishes to a minimum value at 360 μ, as with Coke A. The general level of the shape factors is lower, however, and, possibly for this reason, the rise for smaller sizes is steeper. Both cokes give a σ value of 0.64 at 250 μ. For lower sizes the curve shows two minima, one at 250 μ and one about 140 μ. It is of interest that two minima also occur, near 300 μ and near 100 μ, in the pore wall thickness histogram for this coke (Fig. 3).

Grinder III gives a pattern generally similar to that for Grinder IV but appears to be displaced somewhat towards the finer sizes and towards higher shape factors. The lack of a second minimum may be due to the fact that finer fractions were not available for examination.

The curve for Grinder II shows the most marked divergence both from the other curves for this coke and for the corresponding curve for Coke A. It gives in general the lowest shape factor throughout the range. This agrees with expectation since the grinder operates with closely spaced parallel planes and low recirculation. It should therefore favour cleavage. The absence of this behaviour in Coke A may reflect the difficulty of controlling the setting of the plates, to which the performance of this machine is very sensitive.

For Grinder I the virtually constant σ of about 0.65 between 600 and 140 μ may be compared with the almost constant value of 0.66 in this range with Coke A. The "shattering" produced by this grinder seems to over-rule structural differences between the cokes.

As with Coke A, the curve for Grinder V closely follows that for Grinder III but is displaced towards higher σ values. With this coke, however, the displacement is more marked—approximately 0.05–0.1 on the σ scale. This displacement may be correlated with the higher speed of Grinder V, which increases the tendency to fracture the grains across their largest planes.

The relative differences between grinders for Coke B apart from a possibly anomalous effect with Grinder II are therefore in the same sense as those for Coke A. The differences are, however, much greater in magnitude.

CONCLUSIONS

The preparation of anisotropic coke/pitch graphites on the industrial scale is favoured by

(i) use of coke with large pores and thin cell walls
(ii) use of the minimum proportion of coke fines (say less than about 100 mesh),
(iii) grinding the coke in a mill which is slowly moving and gives low residence time of the coke. Of the industrial types of equipment, crushing rolls give the most anisotropic product.

Part II. The Effect of Shape Factor on Packing Density

INTRODUCTION

The voidage between the particles in an aggregate of powdered coke depends upon:

(i) the distribution of particle sizes within the coke. This controls the extent to which small particles can fit into the interstices between larger ones and is therefore a factor to which bulk density is very sensitive.
(ii) the shape of the coke particles and
(iii) their mutual orientation in the packed aggregate.

The last two factors are difficult to sepa-

rate. The ability to be oriented depends on the shape—this was the basis of the studies described in Part I of this paper—but is not wholly determined thereby, since given particles can be arranged in different mutual orientations by differences in packing technique.

In the present studies bulk densities were measured for different sized fractions of cokes. Fractional voidages were determined from these values and appropriate particle density values. For these measurements the "band-widths" of the fractions were limited by sieving between close sieves such that the ratio of the smaller to the larger sieve aperture was never less than

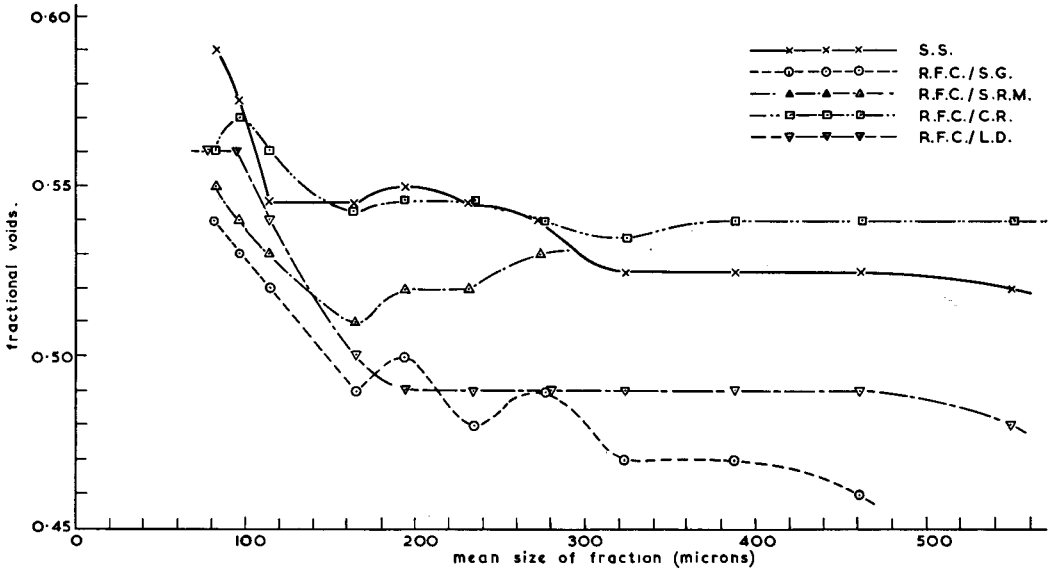


FIG. 6. Voids vs size for coke "A"

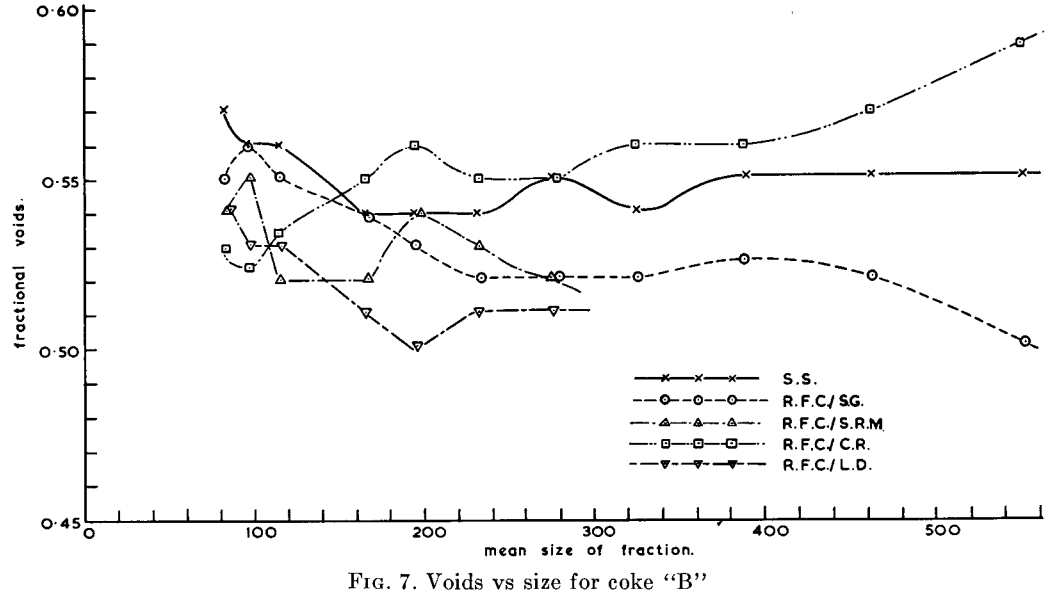


FIG. 7. Voids vs size for coke "B"

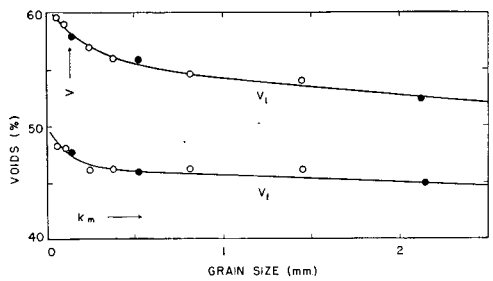


FIG. 8. Relationship between void space and grain size.

objection since the "band-widths" of the fractions used for the bulk density determinations were narrower than those used for the particle density and shape factor measurements. For the bulk density determinations, narrow fractions were found to be essential in order to obtain meaningful results; the particle density and shape factor however were found to vary only slowly with particle size and it was therefore considered justifiable to treat the results in this way.

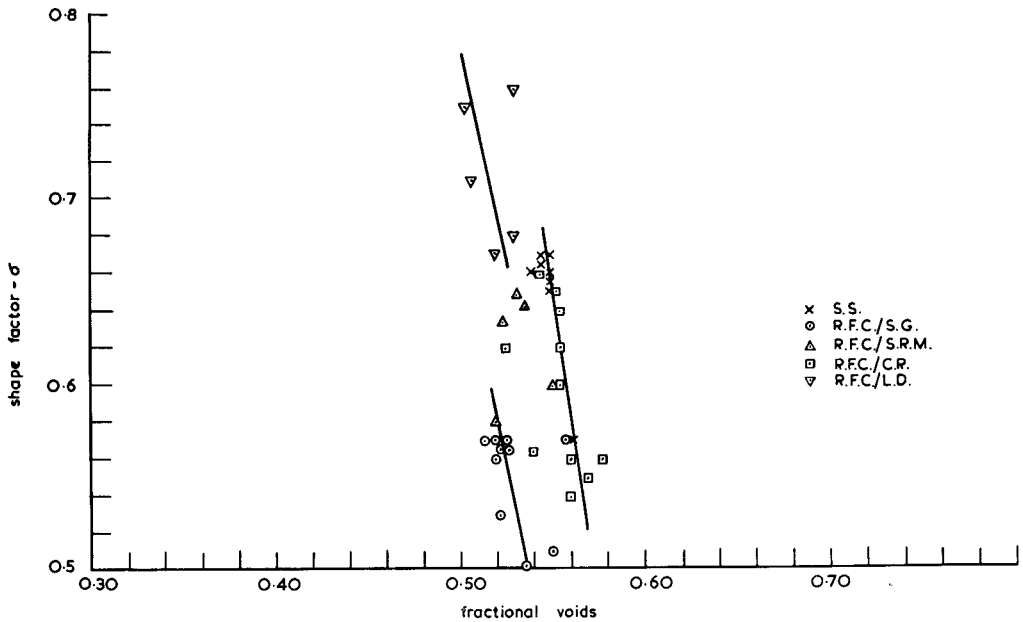


FIG. 9. Voids vs shape factor for coke "B"

0.83. It was hoped by this means to eliminate variations due to differences in size distribution. A carefully standardised procedure was used for bulk density measurements in order to minimise extraneous variations in orientation. The variations in fractional voidages then obtained were examined for correlation with shape factors.

The procedure was to plot fractional voids against mean size of fraction. The voidage values for given sizes were then cross-plotted against the values for the same mean sizes, obtained from the data described in Part I of this paper.

This procedure is open to an apparent

EXPERIMENTAL

Determination of bulk density

Since only small amounts of many fractions were available, it was necessary to use a method which did not require large quantities of powder to obtain the necessary accuracy. The apparatus used was similar to that described by Busby[5]. It consisted essentially of a 100 ml. glass measuring

[5] T. S. Busby, J. Soc. Glass Technol. **34**, 10 (1950).

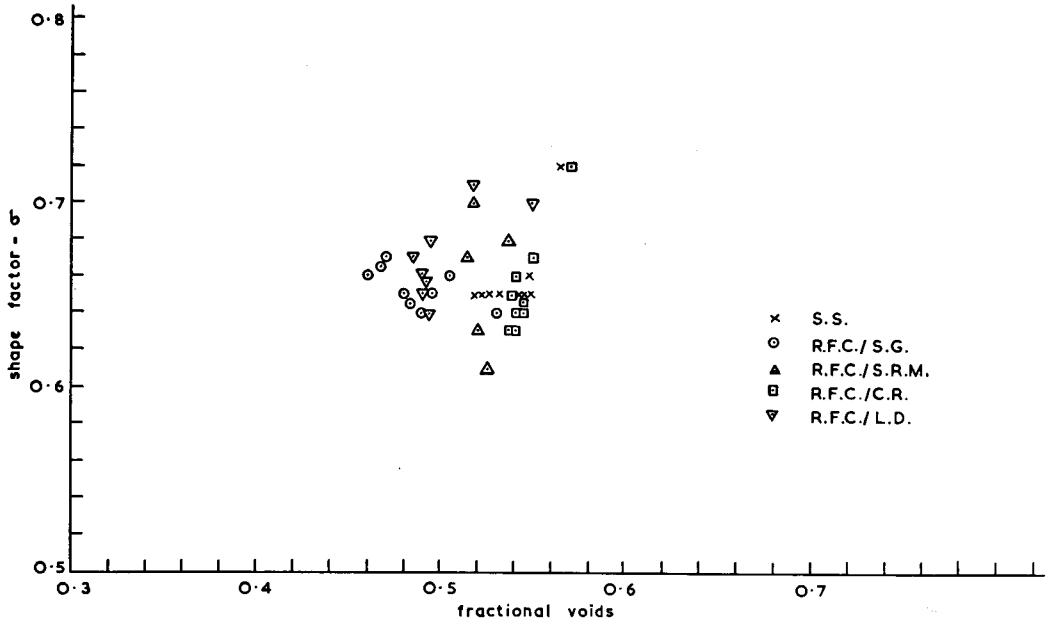


FIG. 10. Voids vs shape factor for coke "A"

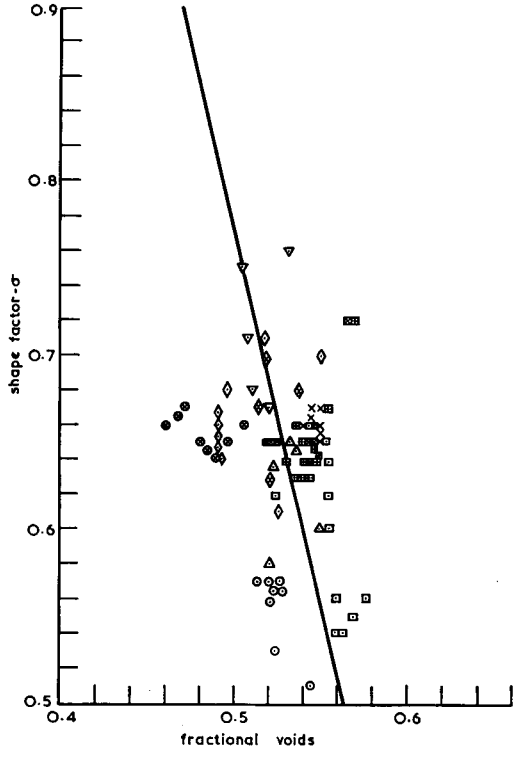


FIG. 11. Voids vs shape factor for cokes "A" and "B"

cylinder held in a metal clamp which was raised by a motor-driven cam and then allowed to fall freely for ½ inch. The cylinder was jolted 70 times per minute and each sample was tamped in this way for five minutes before readings were taken. The results were repeatable within 1 per cent.

Plots of fractional voidage against mean size of fraction are reproduced as Figs. 6 and 7.

DISCUSSION

Evidently, the fractional voidage in a bed of particles is not affected by uniform magnification in all directions; the voidage is therefore, to a first approximation, independent of absolute particle size and only dependent on the distribution of sizes. Andreasen[6] has investigated the validity of this simple principle experimentally for industrial powders. He has found it to hold for coarse particles but for finer sizes the voidage

[6] A. H. M. Andreasen, J. Soc. Glass Technol. **24**, 174 (1940).

rises (Fig. 8). The results shown in Figs. 6 and 7 are in general agreement with this view. They also indicate, however,

(i) departures from the simple curve which seem to be larger than is warranted by experimental error,

(ii) for some grindings, an increase in voids as the size *increases* from about 200 μ,

(iii) a general tendency for the curves to approach the simple Andreasen pattern more closely in those conditions under which the shape factor-size relationship are simplest.

These observations are qualitatively in agreement with the hypothesis of a relationship between fractional voids and shape factor. Fig. 9 shows an attempt to trace such a relationship quantitatively for Coke B. The points lie on a fairly well-defined band but there is also a tendency for the points for different grinders to lie on different, but parallel, lines. This suggests that the analysis is not complete and that shape factor alone is insufficient to account for the residual variations in voidage.

For Coke A, the treatment gives no correlation at all, as is indicated by Fig. 10. The shape factors for this coke are relatively insensitive both to grinder and to size fraction except for the finest particles, as previously mentioned, but there is none the less a wide variation in the voids among the different fractions for the three grinders for which results are available. More detailed examination shows however that most of this variation occurs with fractions obtained from the sample grinder and results in these fractions having anomalously low voids contents. If these points are excluded, the remainder are fairly well clustered. In Fig. 11 all the points for both cokes have been collected and the best straight line drawn through them. This has the equation.

$$\sigma + 4\epsilon = 2.75$$

and if a value $\sigma = 1$, corresponding to spheres is substituted in this equation, the calculated value for ϵ is 0.44. This compares with usually quoted values for random packing of single-sized spheres of $\epsilon = 0.39$–0.40.

It would appear therefore that this correlation of voids with shape has some validity, although there are other factors present which have not been isolated in the experimental work.

This conclusion applies of course only to randomly oriented packings. The extrusion process used in graphite manufacture will orient the particles as previously noted. A low shape factor, i.e. for plate-like particles, particularly under the influence of lubrication by the binder, will give oriented packings with correspondingly low voidage.