THESIS.

A STUDY OF THE PHYSICAL STRUCTURE OF COKE
and the influence thereof on blast furnace practice

Submitted to the University of Glasgow
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for the Degree of Docotor of Philosophy

June, 1950.

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Part One.

INTRODUCTION.

SECTION 1.

COKE IN THE BLAST FURNACE.

In the iron blast furnace coke serves three main purposes. Firstly, it is the fuel of the furnace, providing the heat necessary for the chemical and physical reactions of the smelting process.
Secondly it supplies the reducing agent by reaction with which the oxides of iron are made to yield the metal.
Thirdly coke is generally considered to be very important in maintaining high permeability of the burden to gases, it being the only material charged which maintains its shape and size down to the tuyeres. It must also play an important part in maintaining conditions of high permeability to slag in the bosh.

The behaviour of coke as a reducing agent need hardly be discussed. A large part of the reduction of ores takes place through the agency of carbon monoxide. Direct reactions between coke carbon and oxide of iron will occur in the lower reaches of the furnace where the oxide is present as a constituent of a slag at very high temperature. These reactions will probably depend rather on the nature and composition of the liquid melt and on the temperature than on any property of the coke. Reaction rates will probably be very high.

Work done by Perrot and Kinney (1) in U.S.A. about 1923 showed that combustion occurred in a zone extending to about 40 inches round the nose of each tuyere.

The size of the zone seemed to be independent of the operating conditions of blast pressure and (above a minimum size) furnace diameter.

In general the pattern is the same as that found by Hiles and Mott (2) in their studies of the combustion of coke in fuel beds. The combustion zone may be considered to be in two parts distinguished by gas composition and by the reactions taking place. In the first or "oxidizing zone" there is free oxygen over 1%, nitrogen, carbon dioxide and a small proportion of CO. In the second or "reduction zone" the O_2has been almost all combined, CO_2 is reacting with carbon, and the gas composition changes rapidly until it is almost entirely N_2 and CO.

The details of the mechanism of the oxidation of carbon are rather obscure. Early work has been reviewed by Hiles and Mott (2) who showed how the conclusions reached usually depended on the experimental conditions operating, the study of combustion in beds appearing to be a particularly unsatisfactory approach to the fundamental mechanism of the reactions.

Perhaps the most satisfactory contribution has been by Strickland-Constable (3) who admitted oxygen at very low pressure to an evacuated bulb containing a hot carbon filament. The low pressure reduced the probability of secondary reactions in the gas which could be considered at low temperature. The gas was analysed when time had been allowed for about three-quarters of the oxygen to be used up. Accuracy of analysis was rather low but it was established that the reaction was probably of the first order. He deduced that CO was the product of the primary reaction. This has recently been confirmed by Loon and Smeets (4) who burned spheres of carbon in fast streams of oxygen, that is, under more "normal" conditions. CO_2 must, then, be formed by oxidation of the CO in the gas phase, though possibly very close indeed to the carbon surface and Loon and Smeets suggest a "diffusion layer" enveloping the carbon in which oxygen must pass through newly formed CO to reach the carbon surface.

The net effects of the primary and subsequent reactions is observed as the two zones of combustion described above.

The work of Hiles and Mott covers the effects of different fuels and conditions on the extent and definition of the two zones of combustion and on the temperatures developed. Broadly speaking "conditions of low reactivity" — large sized or unreactive fuel like beehive coke, and low gas velocities — produced a long well defined oxidation zone characterised by a very high maximum temperature at its boundary. On the other hand "conditions of high reactivity" caused by small or highly reactive fuel such as charcoal, or high gas velocities producing very turbulent flow conditions, gave a shorter oxidation zone merging into the reduction zone, a much lower maximum temperature being developed.

The type of combustion zone formed must depend upon the relative rates at which the following reactions can proceed.

(1) $2\ C + O_2 = 2\ CO$ — Primary reaction at C surface.

(2) $2\ CO + O_2 = 2\ CO_2$ — Secondary reaction in gas phase.

and (3) $C + CO_2 = 2\ CO$ — Secondary reaction at C surface.

At combustion temperatures and in the presence of free oxygen, both (1) and (2) proceed rapidly to the right. Reaction (3) would be expected to be ineffective until the oxygen was used up, for the CO formed by it would immediately enter into reaction (2). Under Hiles' and Mott's conditions of "high reactivity", however it would appear that (3) must proceed sufficiently fast that CO and O_2 can exist together in the region where oxidation and reduction zones merge or overlap. The independent variable controlling the relative rates of these reactions seems to be the "reactivity" of the carbon to O_2 and CO_2. This reactivity may depend on one or both of two factors — firstly the chemical properties of the surface as they affect the reactions, and secondly the extent of the available carbon surface and its spatial distribution.

It is not clear that chemical properties are really important. Reactivity can be enhanced in coke for domestic purposes by additions of soda ash which probably has some catalytic action but whether there is any practical difference between the chemical properties of the surfaces of metallurgical cokes of different origin by the time they reach the tuyere zone of a blast furnace seems doubtful. The extent of the surface at which the carbon may be burned depends upon the porosity, and on the pore size distribution in the coke. It is the main purpose of this research to find a method of determining pore size distribution as a first step toward deciding its importance as a factor affecting the utility of coke.

The effect of these considerations on blast furnace operation is difficult to assess. Consensus of opinion is that fuels of low reactivity are most desirable because they suffer less solution by CO_2 in the stack, and develop higher maximum temperatures at the tuyeres. High solution loss of carbon in the stack is of course undesirable from the point of view of thermal efficiency. High temperatures in the tuyere zone may have an important effect on the last stages in the reduction of the oxides of iron and the metalloids and on the conditions in the hearth affecting slag-metal reactions. On the other hand the total volume of the very hot zone is small and the possibilities of heat transfer down to the hearth by radiation limited, so that the importance of this factor may have been exaggerated. Beehive coke of low reactivity has frequently been used in the past as a "medicine" for "sick" blast furnaces but its value may lie in its size and strength rather than in its reactivity. Recently it has been reported (5) that the use of very low porosity coke (of, presumably very low reactivity) led to unfavourable temperature gradients in the bosh which upset the working of the furnace as presently designed. It will be obvious that the true influence of fuel reactivity on blast furnace operation is not yet properly understood.

Supposing however that highly unreactive fuel <u>is</u> desirable, what does this mean in terms of the properties of the coke? Chemical reactivity, may be expected to diminish as the coking temperature is raised. The available surface will depend upon the size of the coke at the tuyeres and the size distribution.

(for smaller pieces obviously present a greater area to gases); it depends to a minor extent on particle shape; and it depends on porosity.

For a given shape and size of coke the "visible" surface depends directly upon porosity. If the porosity is 50% the surface is 1 . 5 times that of a similar particle having no porosity. If the porosity is 40% or 60%, the factor is 1.4 or 1.6 respectively. As these are extreme values it can be said that "visible" surface is itself of little importance.

Mott and Wheeler (6) have shown however that combustion affects the outer ⅛th inch layer of the coke piece so that the surfaces of pores within that zone is also involved. The effective area of internal surface depends not only on total porosity but on pore size or more generally on size distribution, and on the accessibility of the surfaces of these pores to the reacting gases. Mott and Wheeler (6) have asserted that the permeability of coke is negligible but it is not zero and may well be one of the more important variables differentiating cokes of "good" and "bad" quality.

Discussing the effect of porosity per se Mott and Wheeler have reported that highest temperatures were obtained from cokes of highest porosity — but that a certain coke of only 40% porosity also gave very high temperatures. Recent work already mentioned however (5) suggests that in the blast furnace at any rate, low porosity gives low reactivity and high temperatures, and though the truth of the matter is obviously in some doubt, that is the assumption that will be made here.

Pore sizes, following the above assumption, should be large in order that their contribution to surface area be small. Pores should be un-connected and permeability low.

The assumption made must of course be tested by experiment, and it is the purpose of the present work to contribute to the solution of the many problems invloved. It is generally considered that porosity should be high. The reason for this is not clear but may be concerned with the maintainance of high coke volume in the charge with a view to high permeability of the burden to gases. No successful large scale correlation of porosity against blast furnace performance has been carried out. This task would be very difficult in view of the complexity of factors from which this one would have to be distinguished.

The rate at which carbon is consumed at the tuyeres controls the output of the furnace and is limited by other factors than those considered, depending immediately upon the rate at which oxygen can be supplied through the tuyeres. This in turn is limited by the permeability of the stock through which the products of the combustion must escape from the tuyere zone. Permeability depends on size and size distribution of the materials charged and on the way they segregate when they come off the bell. As coke comprises between 50% and 70% of the burden volume, and as coke alone maintains its size and shape down to the tuyere level, it is clear that factors affecting the permeability of coke beds, namely coke size and size distribution and their stability are of great importance. Large size and close grading are therefore considered to be desirable. This applies equally to ores too, but after they melt in the bosh the coke alone must be sufficiently permeable both to ascending gases and to descending liquids. It seems to be particularly important that the proportion of breeze sizes (under $\frac{1}{2}$ inch) be low. Such small coke tends to accumulate in the hearth and creates unfavourable conditions. Its effect may be to restrict the passage of liquids to the hearth, and possibly to screen it from the heat in the tuyere zone too. It is not clear why such small material is not rapidly consumed.

Size and size stability can be maintained high only by ensuring that the coke is "strong" enough to resist the mechanical forces to which it is subjected during transport and within the furnace. The factors influencing the natural size distributions found in broken coke are not understood, but close grading is usually imposed by screening out fines.

Physical properties affecting size and strength are "hardness" and freedom from fissuring. To some extent these are mutually incompatable, for high hardness can be achieved by employment of high coking temperatures which usually produce a small highly fissured coke. Another property which may be important is the structure of the cells and the thickness of their walls. These are functions of porosity and its size distribution. The possibility of actually measuring hardness, tensile strength or elastic moduli of coke-carbon seems very remote.

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The following summary has been made of the properties probably desirable in a good metallurgical coke.

PHYSICAL PROPERTIES.

Size: Large within limits and grading close.

Strength: High both toward shatter and abrasion to keep size up and fines down.

Real Density: High - <u>if</u> this means harder or less reactive fuel.

Porosity: Low, with a view to low reactivity. (This view is not generally accepted)

Bulk Density: Low, but in virtue of close grading, <u>not</u> high porosity.

Pore Permeability: Low - if possible to control it.

Cell Walls: Probably desired thick.

CHEMICAL PROPERTIES.

Moisture, Sulphur, Ash: All low, and steady. The effects of these on metallurgical load are largely calculable.

Volatiles: Low - corresponding to high density. Effect in furnace of volatiles per se is probably small.

Reactivity: Low.

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The extent to which these properties are separately important is largely a matter of conjecture, and some of them have not yet even been measured. The present research will concentrate on porosity and its size distribution as they may affect reactivity and strength. It will not proceed to correlation with furnace performance, but will, it is hoped advance toward that end.

Section 2.

THE SAMPLING OF COKE.

The aim of the present work is to contribute toward the the better understanding of the properties desirable in blast furnace coke by attempting to measure pore size distribution and to decide whether it is really an important factor and if so, how it operates.

All of the other properties listed at the end of Section 1 except cell wall thickness and pore permeability are regularly determined, many on a routine basis. Attempts to correlate these properties with blast furnace performance have met with little success. This is in large measure due to the inherent complexity of the problem in which the number of variables is large and their degrees of inter-dependence obscure.

One unavoidable difficulty is that coke is essentially a very heterogenous material and is therefore subject to severe sampling errors. This heterogeneity is a consequence of the method of manufacture and although modern coke oven operation aims at the production of the most uniform coke possible, there are limits to what is possible, and these are not always attained.

Examination of any oven-load of coke reveals a wide variation in the appearance of the individual pieces. There are differences in colour, size and shape; apparently in strength and in degree of fissuring; in porosity; and in the gradation of colour from end to end. Nevertheless there is a general similarity in the product of any one battery which frequently marks it as a different coke from others made elsewhere.

The various differences listed can each be attributed to one or more of the following causes.

(1) The temperature gradient across the oven and its variation at different parts of the oven due to
    (a) boundary effects at doors, sole etc.,
    (b) differences in the packing of the charge.

(2) The variation in the packing of the charge from the bottom to the top where the fall of the coal is greatest and least respectively will have three effects.
    (a) The temperature gradient and hence the rate of heating of the charge and the porosity of the product will be affected.
    (b) porosity may be affected more directly by the varying resistance to swelling in different parts of the charge.
    (c) (a) will lead also to different final temperatures in different parts.

A smaller variation in packing density will occur from end to end of the oven it being higher at any level immediately under the charging holes.

(3) Accidental or unavoidable variations in oven wall temperature.

(4) The effect of wall taper which though only about 2" is 12½% on a 16" oven.

(5) The possibility of inadequate mixing of the constituent coals cannot be ignored.

Variations also occur between ovens due to changing blend, upsets in time schedules and normal temperature differences.

These local variations in coke quality may have little effect on the usefulness of the fuel in the furnace but are always important when samples are being taken for any test. Samples must be truly representative of the batch being tested, and the quantity subjected to the test sufficient to ensure that the mean value of the index sought is obtained with suitable accuracy. It is frequently impossible to attain a desired accuracy without employing inconveniently large samples. The size of sample required can usually be determined by statistical methods, and sampling technique planned accordingly. For example, in determining the size distribution of certain cokes the author found that a sample of 20 increments, each of 50 - 60 lb. weight — that is about half a ton of material—was necessary if average size was to be determined correct ± 0·1". As the total range of size being obtained was less than 1·0 inch, it will be appreciated that sample size was limited by practical considerations and not chosen as being adequate for requirements of accuracy.

Data are often averaged over periods of a week or a month in order that differences between periods may become significant, and large scale correlation work must certainly be organised on a long term basis if really significant results are to be obtained . There is probably wide scope in the industry for the application of the more advanced statistical methods popularly known as "operational analysis".

The present work has been carried out largely by classical methods, with elementary statistical safeguards. When new methods were being considered the importance of sampling was recognised. Preference was given to methods which could be applied to reasonably small quantities of broken coke such as could be obtained from a larger "fair" sample by standard coning and quartering technique. Methods invloving examination of specimens — by the microscope for example — were avoided because of the serious sampling errors inevitably incurred. The determination of apparent density is a notable exception to this rule. A suitable method using a "fair" sample could not be found but the opportunity was taken of making a careful study of the sampling errors obtained.

Throughout the work, where errors are estimated by statistical means, they are assumed to be distributed normally about their mean M and the range quoted as $M \pm \epsilon$ % (where $\epsilon = 2$ X the standard deviation) is that within which 95% of values are expected to fall. It was not always possible to apply these methods rigourously and in certain cases accuracy estimation is less reliable.

The materials used are in this research listed below in Table I with Code Numbers and notes on their origin. Sampling was not under control as cokes were ordered by letter from various parts of the country. The selection is geographically fairly wide, but the similarity among I, II, and IV on the one hand and VI and VII on the other may be useful in raising the significance of any differences found between these groups. It was hoped that the inclusion of a beehive coke might yield information on the alleged superiority of that type as a metallurgical fuel. The other important differences are that VI was made in rather old wide ovens and that II was of very low ash content. Coke P had very large pores and was included as an extreme case of a porous material like coke, while the Quartz Q representing the other extreme, has been employed at various stages of the work as a standard non-porous material.

A preliminary to the measurement of pore size distribution must be the determination of absolute porosity. This has led to investigations into the measurement of apparent and real densities and to an attempt to measure the apparent density of small particles (as opposed to their real density) by a new method displacing a plastic material. This part of the research is reported in Part II.

In Part III are considered various methods which have been investigated for the determination of pore size distribution, including the successful "counting" method in Section 10. The results of these experiments and the inferences drawn from them are discussed in Part IV, while in the Appendix some subsidiary work on sieving and the details of the real density investigation are reported.

TABLE I. - List of Materials Examined.

Code No.	Source	Appearance.
I	Scottish blast furnace coke from local coals blended 15% Durham coal.	Dull Black
II	Scottish Electrode coke from low volatile coal washed to give very low ash.	Blocky, hard silvery.
III	As II but received a year earlier (Appendix A only)	As II.
IV	Similar to I. Obtained from same ovens about one year later.	Dull black.
V	South Welsh blast furnace coke.	Silvery.
VI	Durham foundry coke from 20" ovens.	Silvery but black inner ends.
VII	Durham beehive coke.	Mixed.
P	Paraffin coke from shale oil residues.	Vitreous black.
Q	Mined quartz with small proportion of muscovite present.	
C	Household coal.	

Part Two.

THE POROSITY OF COKE.

SECTION 3.

THE ORIGIN OF PORES.

Before discussing the measurement of porosity a short account of the formation of pores in coke may be desirable especially as the results of the research do have an important bearing on coking mechanism.

The origin of porosity is of course bound up with the mechanism of coking and this is not at present well understood. Generally accepted theory suggests that coking coals become soft between 350° and 450°C due to the "melting" of some easily fusible components or decomposition products (of unknown nature) and dispersal of the infusible part in the melt to form some sort of colloid of plastic consistency. Further decomposition of the fusible material is then supposed to form gaseous products which form bubbles and cause the coke to swell if the gases evolve faster than they can escape from the mass. Elimination of the fusible component by decomposition leads to re-solidification of the swollen char with enhanced carbon content.

Recently Berkowitz (8) has criticized this theory adversely, mainly on the grounds that there is no experimental evidence of the fusible component and that in any case carbonizing coal does not really behave as if such a component were formed. In particular, he says, that initial melting of the component would be expected to be accompanied by a shrinkage as the liquid occupied the pore space which is about 5% of the volume of a coking coal.

He provides an alternative theory which is compatible with the known behaviour of coals of different rank and appears more acceptable, though lacking rigorous proof. Softening is explained as being similar to that of polymeric plastics - for which suggestion there is some empirical evidence. Gas evolution is still considered to be due to decomposition of coal material but the size of pores formed in the coke depends on the degree to which the coal has softened and on the pore structure of the parent coal. This is believed to be highly constricted and hence less permeable to gases, in the so-called coking coals than in those of higher or of lower rank, and the formation of the familiar bubble pores in coke is due to the gases being evolved faster than they can escape via the existing pore system. Non-coking coals do not swell and do not develop high porosity either because they are deficient in volatiles, or because the volatiles can escape easily through a permeable pore system in the coal.

In this explanation pores are depicted as being formed <u>within</u> the particles of coal. Softening, however, combined with the mechanical pressures developed due to swelling in a confined space must promote the coalescence of the coal particles and this presents the possibility that bubbles form also <u>between</u> the original coal particles. Indeed Bangham, McKee and Pirani (9) have shown by heating together ground glass and alkaline earth carbonates that if the glass softens before the salt decomposes a pore structure like that of coke can be produced.

It seems probable that both mechanisms operate and that their relative importance will depend on the relative rates of softening and gas evolution. The pore size distribution obtained will be shown to be compatible with this suggestion.

SECTION 4.

THE APPARENT DENSITY OF COKE (D_a).

The literature on the measurement of the apparent density of coke has been reviewed by Reif (10). The meaning of the term as it applies to porous material is discussed, and it is very properly defined as "the ratio of the mass to the geometric volume of a representative cube of the material". Thus any porous material with a definite upper limit of pore size has a definable apparent density but its measurement depends on the production of a "representative cube". This sample need not be cubic. Any geometric form bounded by "smooth" surfaces would be equally suitable. The essential feature is that the volume can be uniquely defined.

The surface of broken coke is not "smooth" in the special sense that the rims of the open pores are not uniplanar so that there is no unique definition of the bounding surface of the particle, and hence its volume is uncertain. This uncertainity is proportionately less for larger particles and tends to zero for particle of infinite size. A representative cube may be regarded as a portion of an infinite particle such that if an infinite number of similar cubes were built into a single mass the apparent density would not be altered.

Apart from the "boundary" errors described above, the measurement of D_a is subject to sampling errors, size degradation errors and the error of determining fissure volume as pore volume.

Sampling errors can be reduced to any desired level by taking more and more pieces in the sample. For convenience this usually means taking smaller pieces but it is not always practicable to do so. Small pieces of coke are subject to a variance due to position in the original pieces, so that the number of small pieces must be large enough to cancel this new error.

Size degradation errors are negligible as long as the pieces are much larger than the largest pores.

Fissure errors can be minimized only by rejecting badly fissured pieces from the sample and that usually limits the size of pieces that can be used.

The normal method of determining D_a is by a soaking or boiling method which may be applied either to half oven width pieces (6) or to broken lumps of 3" - 4" size (7). Briefly, a weighed mass of coke is soaked in water and then re-weighed in water and again in air after draining. From these three weights the apparent density can be calculated.

Reif has shown that such methods are very inaccurate, yielding values 5 or 6 per cent <u>higher</u> than those obtained by a "geometric" method. The discrepancy is due to the failure of the water/air interface after draining to coincide with the statistically "true" boundary of the lumps. If the position of the surface as defined by the water/air interface under (more or less) standard conditions is in error by say $\frac{1}{32}$" then the error in density will depend upon size, being 4½% for 4" lumps; 9% for 2" lumps; and 18% for 1" lumps. This error is severe and certainly discourages attempts to measure D_a on small pieces, no matter how much better the sampling may be.

It was decided to work directly from Reif's definition and employ the following geometric method. About 25 pieces of coke were taken from the gross sample as randomly as possible but badly fissured pieces being rejected. A specimen was cut from each piece with a diamond edged cutting disc. The specimen was to be bounded by plane surfaces; was to be as large as possible from the parent piece; and free of all but the finest fissures. These specimens were dried, dusted and weighed, and then soaked in hot paraffin wax, taken out and cooled. A re-dip in cooler wax was usually necessary in order that each piece should be completely enveloped and the wax firmly attached to the coke surface. A razor blade was then used to clean off the excess wax down to the level of the plane surfaces bounding the specimens. The volume of the coke was then determined by the displacement of methylated spirits from a Eureka can. Alcohol was used in preference to water because (a) some pieces of coke floated in water and (b) air bubbles were less likely to cling especially where it had been necessary to clean wax out of a slight fissure on the coke surface.

This technique avoids boundary errors and degradation errors a-lmost entirely, and fissure errors are believed to have been reduced to a minimum. The apparently crude measurement of volume was subjected to repetitive checking and found to give good reproducibility. The pieces used had each a volume of 50 - 100 ccm. and the percentage error in the measured volume of 25 of them was very small. The sampling error however has been found to be very large, incorporating no doubt the variance due to the position of the specimen in the original piece, and that of the piece in the oven, (not to mention the differences between ovens).

The overall variability was examined by determining the apparent densities of individual pieces of the samples of IV and VII. The data obtained are presented in Table II which indicates that errors are probably distributed normally and that when a sample of 25 pieces is used as suggested the mean value of D_a is subject to an error of 2.3%. To halve this error it would be necessary to prepare 100 specimens! This confirms Reif's analysis of Mott and Wheeler's data on some 900 full length pieces representing 200 varieties from which the corresponding reproducibility in D_a from a sample of 25 pieces has been calculated to be 2.2%.

The magnitude of error obtained is in itself of considerable importance as it is impossible to envisage a more accurate direct method for determining apparent density, than that described above. The use of larger pieces would reduce sampling errors at the expense of fissure errors. The use of a significantly larger number of pieces would be justified only in very special cases such as the calibration of some indirect method.

Table II. - The Accuracy of D_a.

Coke	Individual Values of D_a.	Mean D_a	Std. Dev.	% Error *
IV	0.746 0.800 0.814,0.818,0.823 0.830,0.843,0.848 0.850,0.854,0.855,0.856,0.864,0.874. 0.875,0.883,0.888,0.890. 0.910. 1.005	0.862.	0.056	±2.3%
VII	0.786. 0.834,0.840,0.848. 0.850,0.859,0.865. 0.900. 0.934,0.935.	0.865	0.043	±2.0%

* On a sample of 25 pieces.

The values of D_a obtained for the cokes examined are given in Table III. The cokes selected have a wide range of apparent densities which can be deduced from later data due to wide differences both in porosity and in real density.

TABLE III. - Apparent Densities and their Relationship with Bulk Densities.

Coke	I	II	IV	V	VI	VII	P	Q
D_a	0.88	0.78	0.86	0.92	0.995	0.88	0.54	2.65
D_b	-	0.455	0.505	0.54	0.56	0.495	0.305	1.43
R D_a/D_b	-	1.72	1.71	1.71	1.78	1.78	1.77	1.85

The development of a method in which a fair sample of broken coke could be used would be very desirable, and a suitable indirect method which could be calibrated by the above direct method can now be suggested. In Table III are given the values of bulk density (D_b) and a ratio $R = D_a/D_b$. The determination of D_b is the subject of Section 11, and the values given are those obtained from large sizes (above $\frac{1}{4}$ inch) of each coke, where D_b is practically independent of size. The ratio R is not quite constant and may depend upon the shape of the coke particles, as is discussed in Section 12. Nevertheless, if the mean value of R= 1.74 is used, then values of D_a=1.74 D_b are all within 3% of the values obtained by direct measurement. When it is remembered that values of D_a are themselves liable to a sampling error of over 2%, it seems probable that the simple relationship $D_a = R\ D_b$ could provide the basis of a suitable indirect measurement of apparent density. Accuracy better than ± 3% would have to be assured of course but could probably be attained by standardization of method and careful determination of the best value of R under the standard conditions. R might be made more constant for different cokes by modifying the particle shape by trommelling the sample.

SECTION 5.

THE REAL DENSITY OF COKE (D_r).

It is obvious that the total porosity of coke can be calculated from the values of its apparent and real densities. The real density of a porous material may be defined as the ratio of its mass to its volume excluding the volume of all pores. The measurement of real density thus defined therefore depends upon the possibility of filling all the pores with a suitable displacement fluid.

Previous studies of real density determination have shown that pores exist of sizes probably down to molecular dimensions and that to fill them is not an easy matter, Densities obtained by displacement of helium are generally accepted as being most nearly correct but that method was not available. The use of liquid displacement media have never been found very satisfactory as different liquids give different values of density for the same coke. Until recently no satisfactory theory had been put forward to explain irregular results obtained.

A series of experiments has been carried out to determine if possible the most suitable method of measuring D_r for the purposes of this investigation of porosity. As the details of these experiments and most of the conclusions drawn are irrelevant to the main theme of the research the account of them has been put into an appendix (A). The important conclusions and results are summarized below.

(1) It was confirmed, by inference, that very small pores possibly down to molecular dimensions, do exist in coke.

(2) The method preferred as giving the most consistent results from coke to coke is that using benzene as the displacement medium after a degassing treatment at 500°C. The values thus obtained may be rather lower than by helium displacement but the discrepancy is probably small and very similar from one coke to another.

(3) The values of the real densities of the cokes studied as obtained by the preferred method are given in Table IV along with real densities of Quartz, Paraffin Coke and Coal obtained by displacement of water.

Table IV - Real Densities to be employed in Porosity Calculations

Material.	Method	Density (gm./ccm)
Coke I	Evacuation and Benzene	1.88
Coke II	: : :	1.94
Coke IV	: : :	1.885
Coke V	: : :	1.965
Coke VI	: : :	2.01
Coke VII	: : :	1.88
Coke P	Boiling with Water	1.445
Quartz Q	: : :	2.65
Coal C	: : :	1.33

SECTION 6.

Intermediate Densities by Diakon Displacement (D_d)

The presence of minute pores, possibly of molecular dimensions has been inferred from the results of the experiments on real density of coke.

When the pore size distributions reported later were measured it was found that no pores smaller than 0.04 mm were being detected. At the same time it could be deduced that the (counting) method used was probably failing to record a small proportion of the porosity.

These considerations pointed to the desirability of investigating these smallest pores. It was decided to attempt to measure the apparent density of cell wall material in order to determine the amount of any such porosity that it might contain. The following method which has been developed employs diakon as the displacement medium.

Diakon is a thermoplastic material which can be moulded with high pressure at temperatures of 120 - 140° C, and which is used for mounting specimens for metallographic examination. It is used here as the displacement medium in density determination in the belief that it does not penetrate the finest pore structure of the coke.

One gram of coke (or a similar volume of other materials) was mixed with about 8 ccm. of diakon powder and placed in a 1" diameter cylindrical steel mould with a thin layer of diakon above and below. The mixture was moulded at 4000 lb. per square inch pressure applied as the mould heated up from 90° to 130°C and maintained during cooling back to 40°C. The density of the composite moulding was found by the method of Archimedes. The density of diakon alone prepared in the same way was determined separately, and the value of the density D_d of the coke by the displacement of diakon was calculated. Densities were adjusted to the basis of that of water at 25°C equal to one to be in line with the real density data. The average of four tests was shown to be necessary that the accuracy of the mean should be within ±1/2% - as it is for real density.

The data obtained in a series of experiments using this method are collected in Table V.

The figure obtained for the density of quartz demonstrates the accuracy of this method for non-porous material but the degree of penetration of diakon into pores under the conditions of the test must be deduced from a study of the data obtained. The values obtained for coke are all considerably lower than the real density figures, showing that there are some pores which have not been penetrated. It is important that the nature of these be discovered, and particularly whether they are being included in the distributions being measured.

Diakon has a very large molecule, being a polymer of methyl methacrylate. It has a high viscosity too and these factors favour poor penetration. But moulding is carried out at high temperature and very high pressure both of which favour penetration of pores.

TABLE V. - Diakon Densities. (D_d)

Material	Size	Pressure	D_d	Remarks
Quartz Q	60/100m.	4000lb/in^2	2.655	D_r 2.650
Coal C	85/100m.	4000 :	1.26	D_a 1.25, D_r 1.33.
Coke I	100/120m.	4000 :	1.815	
Coke I	100/120m.	2000 :	1.81	
Coke II	100/120m.	4000 :	1.91	
Coke II	72/85m.	4000 :	1.885	
Coke IV	150/170m.	4000 :	1.76	
Coke IV	-72m.	4000 :	1.76	
Coke V	100/120m.	4000 :	1.86	
Coke VI	100/120m.	4000 :	1.88	
Coke VII	100/120m.	4000 :	1.815	
Coke P	100/120m.	4000 :	1.39	

The increase in D_d between coke II at 72/85m. and at 100/120m. demonstrates that even at 4000 lb/in^2 diakon cannot penetrate the small pores in 72/85m. coke. This was confirmed by microscopic examination of the mouldings. The few visible pores present in the smaller size were, however filled with diakon so that poor penetration of bubble pores does not effect the values obtained of cokes of sizes less than 100 mesh.

The figure obtained for coal shows that there is little or no penetration by diakon of pores of the kind found in coal. These are intermicellar pores of dimensions of the order of 10 - 40 Å (35).

The identical values obtained for 150/170m. and -72m. samples of coke IV show that pore space not entered by diakon is not being opened up by further pulverization. The -72m. material is largely very fine dust, and gives a much higher density determined by boiling in water, than 150/170m. coke. (c.f. Fig.14).

The almost identical values obtained for Coke I using 2000 and 4000 lb. per square inch pressure suggests that the pores not entered are not in a continuous distribution with those (if any) which have been filled, otherwise the doubling of the applied pressure would surely have effected some noticable increase in penetration and hence in the value of the density.

While it cannot be proved rigorously it seems highly probable that diakon penetrates all but the "intermicellar" type of porosity which according to one modern theory (8) is "inherited" by the coke from the parent coal. These pores will be of very small dimensions but in coal their volume can amount to over 20% though in coking qualities does not usually exceed 5%.

If this is the case the values of D_d will be closer to the D_s at low values of S than the real densities previously determined. They are still higher than particulate apparent densities however in virtue of surface recesses and concavities the volumes of which were originally part of pore volume of the unbroken coke. A closer approximation to particulate apparent density D_s is however very improbable.

The data obtained on the cokes are applied in Section 7 to the determination of porosity and have proved invaluable in distinguishing "bubble" porosity and "intermicellar" porosity. As a consequence the diakon displacement method of measuring density has played an important part in the determination of the pore size distribution of coke.

SECTION 7.

ABSOLUTE POROSITY.

In the light of the experimental work reported in Part II the measurement of the absolute porosity of coke appears to be a most inaccurate and uncertain proceeding. It depends upon the separate evaluations of real and apparent densities neither of which is quite so simple as might be expected.

It is believed that the method adopted for the measurement of apparent density is theoretically the best but practically and especially for a routine test it is slow and laborious, and though it gives a measure of true apparent density it does so within wide error limits which have been adequately demonstrated.

If real density is defined as the ratio of the mass to the volume exclusive of all pore space, of a representative sample of coke its measurement depends on the possibility of filling all of the pore space with a suitable displacement fluid. As there is no certainty that pores do not exist down to molecular dimensions there is equally no certainty that measurement of real density as defined is possible. Franklin (36) has shown that even the helium molecule is probably excluded from some of the pore space in certain cases.

The measurement of porosity is of course subject to all the errors and uncertainties of the real and apparent densities, and there seems to be a case for setting lower limit to the size of pore being considered, or for a classification of pore sizes into ranges - if any suitable system of distinguishing them can be found.

Even if the finest porosity could have no effect on the combustion and strength properties of coke, ignorance of its extent and nature is ignorance of the ultimate fine structure of the coke. The closeness of approach of the carbon atom lattice occurring in coke (as made at higher and higher temperatures) to the known lattice of graphite has not been assessed satisfactorily; not have the dimensions and dispositions of the crystallites or micelles of which cokes is thought to be composed. These problems are in a sense the same. Measurements of both the volume and the surface areas (by sorption methods) of the pore space between these crystallities would assist in the estimation of their dimensions. These have already been measured for coals (11,35).

A possible means of distinguishing the finest of the pores has been suggested in Section 8 where it was shown that diakon did not penetrate all of the pores and the term "intermicellar" was used to describe the small ones not entered. The assertion that they are actually of the same type as those known to exist in coal and derived from them would be very difficult to prove. It does conform with a current theory however, and the volume of porosity involved fits that theory reasonably well. An alternative is that the fine porosity is due to a micro-constituent in most cokes which appears to have "pores" within itself. These look as if they had been formed within a laminated structure of a coal constituent,possibly fusian,and are of sizes up to about 0.003mm. It has not been possible to verify that they are actually pores,and they are of such dimensions that it would have been expected that their penetration would have been facilitated by fine grinding(as to "-72m"). It is not clear why pores of this size and type should be so much more accessible to water say, than to diakon. Their total volume could be estimated by microscope only roughly, but seemed to be very much less than the porosity not accessible to diakon. In view of the general indications from the work on real densities that porosity approaching molecular dimensions does actually exist in coke, it has been decided to class all these pores as "intermicellar" pores meantime but with the reservation that a further classification of them into at least two groups might be justified. It is hoped to make a closer study of the microstructure of coke in the near future when more information on these very small "pores" may become available.

Pores entered by diakon are being called "bubble" pores, it being assumed that they have all been formed by evolution of gas in the plastic coal. The smallest pores which could be distinguished under the microscope as being occupied by diakon were about the same size as the largest of those described above that is about 0.003mm. They were always round; there were very few of them; and they may well have been only small chords of much larger spheres.

Table VI has been prepared to show the total porosities of the cokes used in this work, classified into the two types discussed above. The range of values of "intermicellar" porosity is surprisingly large but is believed to be significant having regard to the accuracy with which D_r and D_d were obtainable. The magnitude of the value bears no obvious relationship to any of the other properties of the cokes, nor to their geographical origins, or methods of manufacture. The occurrence of intermicellar porosity in coke P is of particular interest because in that case there was definitely no "microstructure" type of pore present. Coke P is more like pitch than fully carbonized coke however, and its fine porosity could be of quite a different type from that in oven cokes. Nevertheless it provides additional evidence that porosity not discern-

TABLE VI - The Total Porosities of the Cokes.

Coke	Total Porosity	Bubble Porosity	Intermicellar Porosity
I	53.2%	51.5%	1.7%
II	59.8%	59.1%	0.7%
IV	54.5%	51.1%	3.4%
V	53.2%	50.5%	2.7%
VI	50.5%	47.1%	3.4%
VII	53.3%	51.5%	1.8%
P	62.8%	61.2%	1.6%

ible under the microscope can exist.

The significance of the extent of this very fine porosity as a determining factor of coke quality is obscure.

The immediate practical importance of the differentiation of bubble and intermicellar porosity is that it is a first step in the determination of pore size distribution. The usefulness of the distinction will be apparent when the calculation of pore size distributions is discussed in Section 14.

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The choice of cokes has produced a fairly wide range of porosities which will be of value in their final comparison.

Part Three.

PORE SIZE DISTRIBUTION (EXPERIMENTAL)

SECTION 8.

INTRODUCTION TO EXPERIMENTAL WORK.

The values of D_a D_d and D_r provide the means of calculating total porosity but give little information about the sizes of the pores. These may be estimated by microscopic examination to range from a few millimetres down to a few hundredths of a millimetre, but the proportions of each size have proved very difficult to assess. Except for the preparation of "Rose sections" for visual examination there has been no technique developed for the measurement or comparison of pore sizes although in 1917 Ramsberg and Sperr (12) asserted that the evaluation of the amount of porosity was of no value unless accompanied by observations of pore size and cell wall thickness. They quoted Fulton (13) as having expressed the same opinion as early as 1883. In 1924 Malleis (14) suggested the following classification:-

(1) small cells with thin walls
(2) large cells with thin cell walls
(3) small-medium cells with thick cell walls
(4) large cells with thick walls sometimes themselves porous.

This classification was to be made by visual examination of polished sections without magnification and cannot embrace the very large number of small pores not apparent to the naked eye. No quantitive measure of pore size distribution has yet been made.

Methods suggesting themselves for its measurement include microscope and stylus methods, sorption methods and the mercury penetration method.

Microscope and stylus methods and any others requiring the selection and preparation of specimens are subject to severe sampling difficulties and though these need not be insuperable in special research work they are invariably inconvenient. The wide range of pore sizes expected would lead to the difficulty in microscope work that measurements made at several magnifications would have to be reduced to the same basis. Using a stylus the design and manufacture of a suitable tool would have had to be solved before other difficulties such as trace recording and sample preparation could have been tackled. Sampling was however considered to be the greatest drawback of these methods.

Sorption methods would determine primarily surface area accessible to sorbate, and while they might afford some measure of "average" pore size the meaning of such a term is rather obscure Capillary condensation methods might be applied to the distribution of the finest pores but these methods have been reported unreliable (16) when pore diameter is relatively large.

The method which was found to be most successful is called the "counting" method and is described fully in Section 10. Before it is discussed however short accounts are given of certain other attempts to measure either pore distribution or surface area. The first of these is a dye sorption method with which it was hoped to measure lump surface areas including the surfaces of exposed pores. The second is an attempt to employ the mercury penetration method of Washburn and Bunting (17) particularly in an effort to check the distribution of the smaller bubble pores. The third method described was again designed to measure surface area, being an adaption of the air permeation method of Carman (19) for measurement of specific surface. These are discussed in turn in Section 9. In Section 11 a method employing the rather simple measurement of bulk density is described. It was hoped that this might provide an easier alternative to the counting method.

SECTION 9.

DYE SORPTION, MERCURY PENETRATION, AND AIR PERMEATION METHODS.

The following three series of experiments were carried out in attempts to find a suitable means of measuring pore distribution or exposed surface area. None of them yielded positive results but it may be worth while to indicate briefly in each case what was attempted and why it failed.

The first was an attempt to measure "visible surface" by a dye sorption method. A sample of broken coke about ½" - 1" in size was used. The "inner" surface was blanked off by boiling the coke in benezene or some other organic liquid immiscible with water. The coke was then immersed in an aqueous solution of the dye and the rate of its adsorption measured by determining the strength of the solution on periodic samples by means of a photo-electric absorptio-meter. It was expected that either the total dye adsorbed under standard conditions or the rate of its sorption would be proportional to the extent of the adsorbing surface as defined by the position of the water/benezene interface. It was hoped that the position of that interface might be modified by the use of wetting agents which would alter the contact angle coke/water/benezene.

The choice of a suitable dye presented some difficulty. Methylene Blue has frequently been used for such work but was soon found to react with sulphide in the coke and to change colour. A Solway Sky Blue was found to be strongly adsorbed and was employed, but several others were not adsorbed at all and the possibility of chemical reaction between Solway Sky Blue and coke was never really disproved.

Reproducibility of data was initially poor, but it was obvious that sorption could not be completed in a short time and that the *rate* of sorption would have to be related to surface area. This rate ~~was~~ varied with dye concentration and hence with time, as the solution became weaker. As concentration is obviously further depleted in the proximity of the adsorbing surface than at a distance from it, agitation of the solution was necessary and a periodic flow was arranged by means of an air-lift and a syphon. It was also necessary to ensure that the temperature of the solution was constant as variations would obviously cause the water/benzene interface to advance or recede exposing more or less of the coke surface to the dye. Very constant temperature conditions were fortunately available in a large unused room.

In spite of all these precautions however reproducibility of data remained rather poor. Attempts to find how sorption rate varied with dye concentration were not successful but pointed to the existence of secondary effects which could not be determined. Certainly no simple relationship could be found between sorption rate and surface area even when the latter was the only known variable. Surface area was altered by employing different sizes of coke, but the total bulk of the sample was kept constant.

This approach to the problem showed little promise of success and was abandoned early.

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Another attempt was to apply the mercury penetration method suggested by Washburn and Bunting (17) and later employed by Drake and Ritter (15,16). It was hoped that it might be possible to obtain a check on the lower end of the distribution by this method which can be employed only for very small pores.

The method depends on the fact that the mercury/coke contact angle exceeds 90° and therefore mercury cannot enter capillary pores without the application of external pressure. Penetration is a function of pore diameter and applied pressure and the diameter of the smallest pore entered under a given pressure P cm. of Hg is given by the equation

$$d = 0.05/p \qquad \text{(cms)}$$

Then by using pressures up to 80 cms. which was easily attainable, pores down to 0.006 mm. would be entered, and by varying the pressure the distribution of pore sizes might be found.

As the smallest pores detected by the counting method were about 0.04 mm. in diameter it seemed likely that a check could be obtained on the proportion of pores of the smallest sizes. A suitable apparatus was prepared which gave fairly reproducible results but penetration of the mercury continued at the highest pressures attainable and seemed to indicate a large volume of porosity of sizes down to 0.006 mm. and less. Some blank runs were tried on broken quartz of similar sizes. This material behaved in the same way as did coke. Densities of quartz and of coke by mercury displacement were all low and it was deduced that at the pressure applied, penetration of the voids between the particles was not complete. Ritter and Drake have suggested a lower limit of applied pressure which can be usefully employed as 125cm. of Hg but gave no reason for the figure.

As soon as this difficulty was recognised the experiments were discontinued.

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The third set of experiments (18) was an attempt to approach the problem of pore distribution through measurements of the specific surface of sized material. It was hoped that it might be possible to find a quicker method than the counting method which could be reserved if necessary for calibration purposes. It was argued that the specific surface of coke particles would depend on the porosity as well as on size, and for a given size would diminish with diminishing porosity. Specific surface is proportional to the reciprocal of particle diameters and curves such as that in Figure 1 (a) were expected of the range of coke sizes up to 5/6 mesh.

Specific surfaces were measured by the air permeation method suggested by Carman (19) and in a modified apparatus like that described by Gooden and Smith (20). The permeability to air of beds of coke particles had to be measured and that, with certain other quantities such as the length and cross-section of the bed, afforded a means of calculating specific surface.

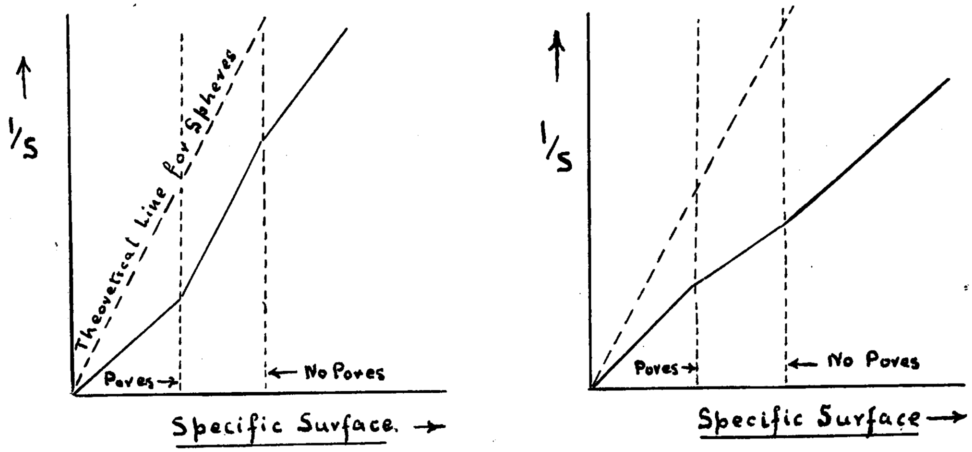


FIGURE 1. - Specific Surfaces by Air Permeation-.
Schematic Relationship with Size S.
(a) Curve expected (b) Curve obtained.

Unfortunately a measure of the voidage of the bed was also required. This could be obtained if the current values of apparent density (D_s) were known, but obviously the method would be valueless if that had to be determined by some other means. An indirect method (19) of deriving D_s was attempted in which the permeability of the bed was measured under different conditions of packing i.e. at different voidages. A value of D_s could be extracted from the data obtained, but it did not correspond with that obtained by the counting method. It varied rather irregularly and in one case exceeded the real density of the coke.

Employing the values of D_s obtained by the counting method the curve in Figure 1(b) was obtained when specific surface was plotted against 1/S. No satisfactory interpretation of this type of curve could be made and this method too had to be abandoned. The anomalous results would seem however to be due in some measure to the difficulty of defining the position of a surface of a porous material like coke. The surface swept by passing air streams is obviously deeper in the particle than that corresponding to the definition of apparent density, so that some of the pore volume becomes confused as voidage. In view of this difficulty which is encountered elsewhere in this research it can be said that the successful application of this air permeation technique to the measurement of surfaces of porous materials like coke is probably impossible.

SECTION 10.

INTERMEDIATE DENSITIES (D_s) BY THE COUNTING METHOD.

THEORY.

The method for the evaluation of pore size distribution will be referred to as the "counting method" and it depends on the following simple theory.

If a non-porous material like quartz is closely sized as for example by sieving, then for any size fraction the average volume V_s of the particles will be related to their average size S by a simple cubic relationship -

$$V_s = k.S^3$$

where the value of k will depend on the statistically average shape of the particles, and on the method of evaluating S (which can be standardized).

Further, their average weight W_s can be obtained as

$$W_s = D_s.V = k.D_s.S^3$$

where D_s is the density of the particles of size S, and will usually be constant for a given material. No evidence can be found in the literature that k should be constant, and indeed a similar shape factor for coal has been shown to change with size (21), but that would be expected of any substance in which the cleavage is much better developed in one direction than in any other. It would seem a reasonable assumption however that isotropic materials whether crystalline or not would tend to break in such a way that the shape factor k would be substantially independent of size, at least within wide limits. In the course of this work considerable justification for that assumption has been found, but only a few materials have been examined and the extent to which it is true or conditions under which it holds cannot be stated.

Now if a porous material is considered a similar relationship will hold but over a certain range of sizes the value of D_s will vary with size from D_a to D_r- from the apparent density of the porous material the real density of the pore wall material, as the pore structure is broken down.

The probability that k will remain constant must, however, be reconsidered for this case. Porous coke, and cell wall material cannot be expected to have identical characteristics but as there is little restraint on the shape of either the large or the small pieces it was thought possible that the total change in k would generally be quite small, and in any case almost certainly gradual. In the absence of an alternative, this assumption was made and it too has been largely justified by results. The variation in k seems to be by only a few per cent in the size range effected.

Then considering k to be virtually constant, the variation in D_s with S can be traced in the size range in which pores are broken down so that at each size an apparent density and hence a porosity may be determined. This porosity P_s will be made up of pores only up to a limiting diameter d_s which will be a fraction of S , for a particle obviously cannot contain a pore larger than itself. In order that the pore distribution may be determined some assumption must be made concerning the distribution of these pore sizes up to d_s in a particle of size S. The only simple assumption that can be made is that the porosity due to any size $d < d_s$ (and expressed as a proportion of real volume) is the same in particles of size S as in the massive material. In other words it is being assumed that no porosity of size less than d_s has been lost in the degradation process. No such porosity can be lost from the interior of the particles but it is always possible at the surface. It will be more probable when d is large and will approach total loss when d equals d_s, but losses of smaller sizes will be partly offset by residual surface porosity due to sizes greater than d_s. Indeed the choice of the value of d_s corresponding to S could - in theory - be made to render the assumption very nearly true. In practice the ratio of d_s to S cannot be fixed primarily to that end, but the error due to the assumption will affect all cokes in a similar manner and it is believed that the pore size distributions will be comparable if not quite exact.

It may be mentioned here that the data obtained in the course of these experiments has been examined to find whether such a loss of porosity occurs outwith the size ranges in which pores are being broken down. That no such loss was detected suggests that it was small and probably negligible and that the above assumption is probably well justified.

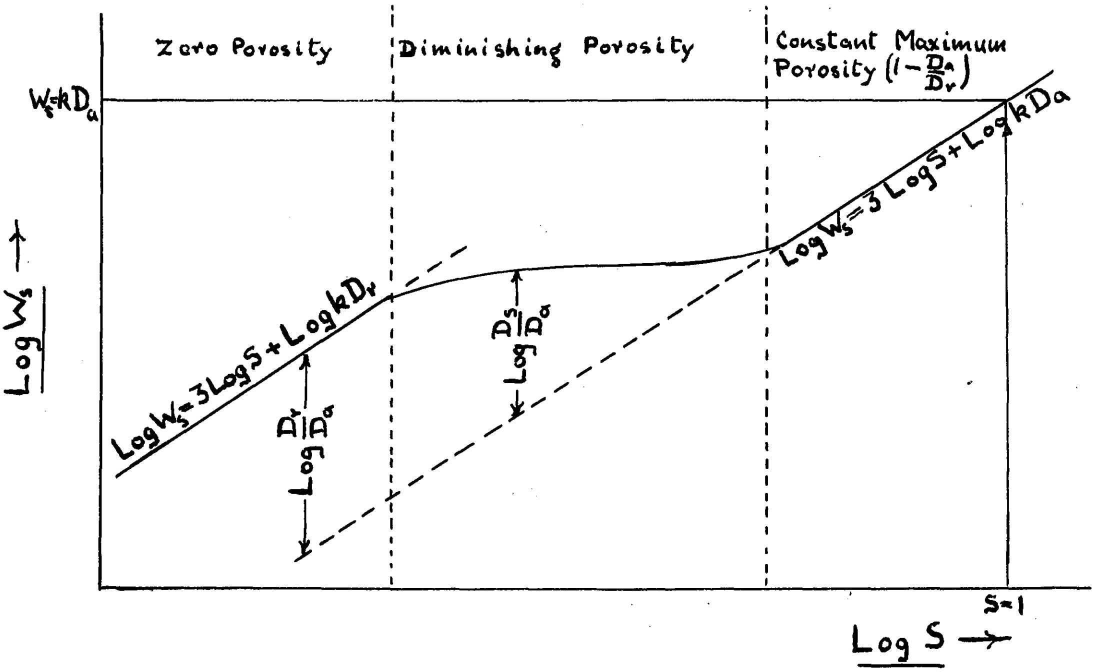


FIGURE 2. - Schematic log W_s/log S curve showing extraction of the Apparent Density Factors D_s/D_a and indicating the evaluation of k.

In order to determine D_s the following method of plotting data has been adopted. If $W_s = k.D_s.\ S^3$, the plot of log W against log. S will be a straight line of gradient 3 as long as D_s and k are constant. Thus when $D_s = D_a$ and D_r, parallel straight lines will be obtained, but in the range of S in which D_s is varying, the curve will lie across the interval between these extreme portions, joining them as indicated in Figure 2.

The total displacement parallel to the log W_s axis has the value log $\frac{D_r}{D_a}$ and the displacement at any size D_s in the range of pore rupture has the value log $\frac{D_s}{D_a}$ (always assuming k constant). Hence if D_a is known D_s and therefore P_s can be determined at any size.

<u>Technique.</u>

In the application of the above theory the following problems had to be considered and they are now dealt with in turn.

(1) The method of comminution of the coke.

(2) The method of sizing the coke, and

(3) the evaluation of S for each size fraction.

(4) The calibration of the sieves used for (2)

(5) The determination of W_s at different sizes.

(6) The accuracy of the method.

(7) The relation between S and d_s.

(1) It was found necessary to determine W_s on a wide range of sizes from about 2" down to about 200m. and it was desirable to standardize the breaking and sampling processes as far as possible. The operation on each coke was carried

out in two stages. In the first the gross sample of about 100 lb. was broken down with a hammer to have a maximum size of about 3". Sizes below 3/32" were screened out and reserved and the larger material screened into as many size fractions as possible W_s being determined on each. The whole sample was then reduced in volume by normal coning and quartering methods, breakage down to about 2" being continued by hammer. Below 2" breakage to $\frac{3}{4}$" was performed in a jaw crusher and then in rolls set at 1/8". To the product was added an appropriate portion of the 3/32" material removed in the first stage. The sample was then prepared for the second part of the sizing operation.

(2) The only feasible means of sizing was by sieving and the development of the sieving technique adopted is discussed in Appendix B. The sizing of large material could not be mechanised but had to be carried out by hand. Above $1\frac{1}{4}$" no wire mesh screens were available and holes had to be cut in stout tinplate for larger sizes. From $1\frac{1}{4}$" down to 1/16" hand screens were used. Except at the smallest sizes in this range hand screening could be completed quite rapidly and efficiently. Below 3/16" however it was evident that the degree of completion of sieving depended upon time, and sieving on the 1/16" screen took so long to near completion that it was seldom used.

Fortunately these screens overlap the range of the B.S.S. fine mesh test sieves which could be shaken mechanically in a Rotap machine. These were used in the second stage of the sizing operation. A part of the sample - $^1/8$" was reserved for real density determinations and the remainder screened roughly at 12m., 30m., 85m., and 200m. The 12m. fraction was coned and quartered until of small enough volume for sieving - about 70 - 80 grams were required. All other fractions were divided proportionately. Machine sieving was carried out on each fraction in turn, each being sub-divided into six closer fractions and undersize which was passed to the next smaller fraction. The 5/12, 12/30, and 30/85 mesh fractions were sieved for three hours and the 85/200 mesh fraction for 5 hours.

(3) There are several "statistical diameters" available for the expression of mean particle size, most of them based on microscopic measurements(22, 23, 24,) . No relationship between these statistical dimensions and sieve apertures has been found and indeed methods using the microscope usually applied to sub-sieve sizes. Hatch (23) has however suggested a method of calibrating sieves by microscopic examination of the size fractions produced in which he assumes the size distribution within each fraction to be log-normal and employs the log-geometric mean M_g of that distribution as the mean size of the fraction. Unfortunately no normal relationship is given between M_g and the sieve apertures possibly because it varies from one material to another.

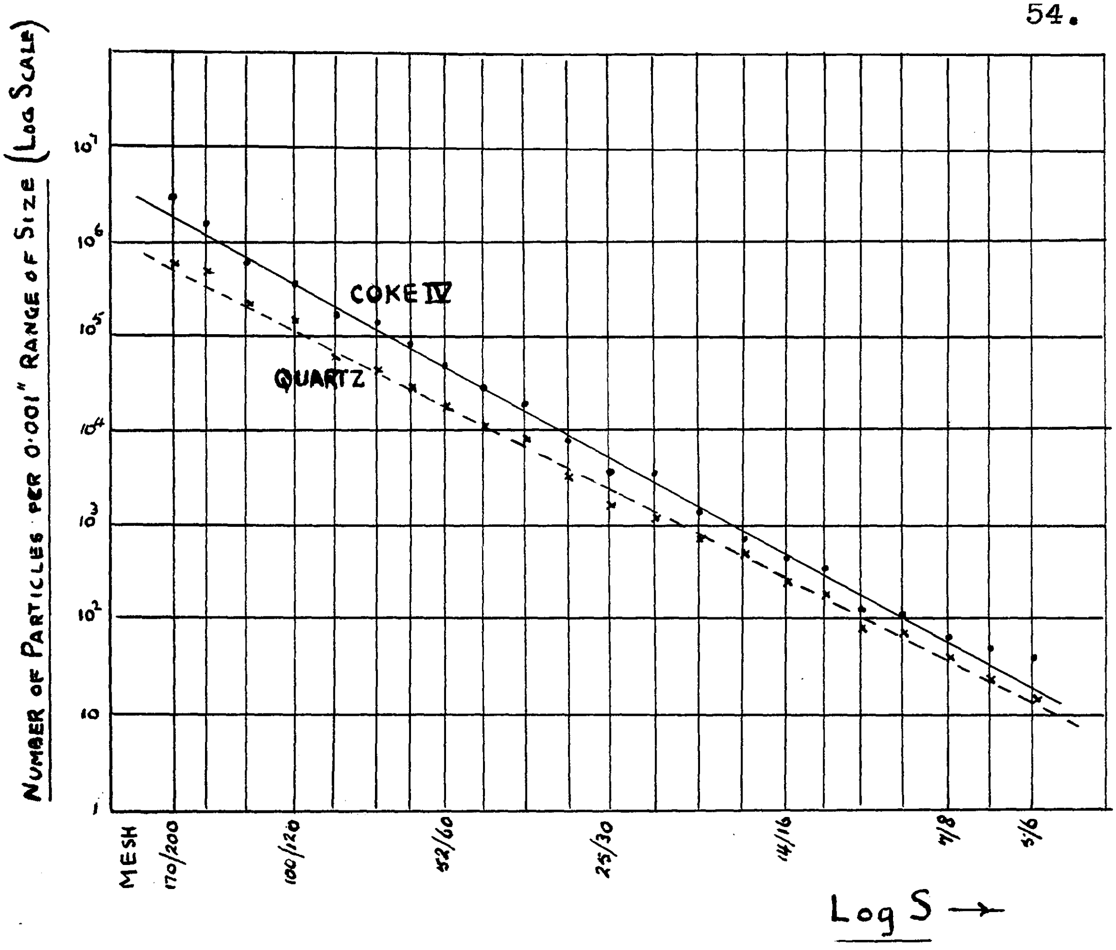


FIGURE 3. - Size distributions by number of particles - Coke IV and quartz.

The simplest and most obvious way of expressing the average size of the particles within a particular size fraction is by the arithmetic mean of the sieve apertures defining the fraction. The validity of the use of this or any other simple relationship between the mean particle size S and the sieve aperture depends upon the distribution of sizes within every size fraction being similar. Closer examination of this requirement shows that for S to be exactly equal to the mean of the sieve apertures, the <u>number</u> of particles per unit range of size must be independent of size. This is a most improbable particle size distribution.

The distributions actually obtained in the samples of Quartz and Coke IV used/in the main experiment were examined. The number of particles N per unit range of size was found to increase rapidly with diminishing size S. These distributions have been found to be rather erratic in spite of careful sampling procedure, but Figure 3 in which log N is plotted against log S, shows that a relationship of the type

$$N = \alpha S^{\beta}$$

holds in both cases, over a wide range of sizes. The values of β were 0.30 for Quartz and 0.32 for Coke IV. From these it can be calculated that in a fraction of size ratio 1.2, the mean particle size is only slightly less than the mean of the apertures, the small difference being proportional to size. The difference between coke and quartz is slight and that between separate cokes probably negligible. An absolute value of S is not required as the chosen value has to be related empirically to pore size at a later stage. It was decided therefore that the mean sieve aperture was a suitable measure of the mean particle size in a given size fraction. The effect of the apparently erratic nature of the distribution cannot be estimated, but it may explain why erratic values of W_s have occasionally been encountered.

The alternative, to follow a method such as that of Hatch would have involved the use of his more elaborate technique and in applying it to the present work it is doubtful that it would have yielded more useful results.

(4) Early work yielded some very irregular curves, especially at the smaller sizes. The accuracy of the sieves was questioned and the inspection of the specification for their manufacture (B.S.S. 410. - 1943) indicated that this was a likely source of the discrepancies encountered. Owing to difficulties in the manufacturing process the cloth cannot be woven to very close specifications especially in the case of finest meshes.

It was obviously necessary that the screens should be calibrated. Several methods have been suggested. The most direct is by microscopic examination of the cloth but the frequency and distribution of oversize apertures is a poor indication of the proportion of oversize particles that will find their way through in a given time. Direct comparison with a Master set of screens is useful for some purposes - but requires a suitably calibrated Master. The method of Hatch is probably the most satisfactory, but it is not certain that his technique would apply equally to all materials because of its dependence on the distribution of size within the size fraction. In any case it calibrates sieves in terms of certain statistical diameters obtained from microscope measurements of particle size which cannot readily be applied to the calibration of the larger sizes. Another possible method is to use "standard powders" which are known to break down to give a logarithmic size distribution (25). Apparent deviations in this law can be attributed to errors in screen aperture. It is doubted if the reproducibility of sampling and screening is good enough to justify the use of this method. It might give different calibrations against different sieving times or methods, and the optimum conditions for the standard distribution might not suit the work in hand.

The method adopted was chosen because of its similarity to the work in which the screens were to be used. A constant value of density and shape factor k was assumed for quartz, and deviations from a straight line of gradient 3 when log W was plotted against log S were attributed to screen errors. Quartz was broken down by a method similar to that specified for coke, being crushed finally in rolls set at $^1/8''$. It was screened by the same method as coke and the average weight per particle determined by the methods described for coke below. Log W_q was plotted against log S in Figure 4 (in back pocket). A good straight line of the expected gradient was obtained from 5m. down to 60m. but at all smaller sizes W_q was larger than was required to bring the points on the same line. This was very much as expected both from consideration of the irregular early data, and from inspection of the tolerances specified. It will be appreciated that only the oversize apertures are effective in producing screen errors; undersize apertures are simply inoperative. It was not proven however that k the shape factor was constant though constancy of the density with size was easily demonstrated. Data became available however for coke P in which porosity was practically zero below 25m.. The lower part of its log W/log S curve is drawn alongside that of quartz in Figure 4 and it is readily seen that the curves are very similar in shape - straight, down to 60m., and then curved upwards. The divergencies were not equal for Q and P in all cases. The mean of the corrections indicated by them has been applied in each case. The correction was made graphically and the constructions have been included in Figure 4. Deviations from the standard line at sizes greater than 60m. were random and considered to be as likely due to size sampling errors, poor sieving reproducibility, and counting inaccuracies as to sieve errors. They were noted in case the same sizes gave irregular points when coke was being tested. Actually they did not, but one other size 30/36m. did give consistently high results which were given due consideration when curves were being drawn. So in a sense the method can be self-calibrating.

The larger screens ($^{3}/32$" - $2\frac{3}{4}$") could be calibrated only by measuring direct with a standard scale. Corrections where necessary have been incorporated in the various graphs drawn. Parts of the curves determined by the two sets of screens overlapped very well and this method seems to have been sufficient.

(5) To determine W_s a known number of particles must be weighed - a simple enough operation when the particle size is large. At —— sizes down to 36/44 mesh the fraction was coned and quartered down to about 1000 particles which were counted and weighed. Sizes 44/52 and 52/60 mesh were dealt with as above but 2000 particles counted so that the total weight should not be so low as to incur an appreciable weighing error.

The extension of this method to smaller sizes was impossible because firstly they were too small for accurate ennumeration with the naked eye, and secondly a much larger count would have been necessary in order that the total weight could be obtained with sufficient accuracy. The following technique was developed which enabled W_s to be determined down to 170/200 mesh.

A counting board was prepared, a ten inch square of inch and tenths graph paper being mounted on a stiff card trimmed to fit exactly. One hundred sampling areas, one in each of the one hundred, one inch squares on the board, each 0.3" x 0.4" in size, were marked off.

A suitable portion of the size fraction being tested was obtained by coning and quartering. It was scattered over the board, spillage over the edges being caught on white paper and rescattered until of negligible proportion. The coke was scattered from a relatively coarse sieve with a mask of paper with about a dozen quarter inch holes in it lying on top of the cloth. This sieve was shaken over the board and gave a fairly uniform distribution of particles upon it.

The number of particles in each sampling area was then counted using a magnifying glass of suitable power and this sum multiplied by 8.33 to give an estimate of the total number on the board. The board was then swept clean of coke which was weighed.

Particles lying across the boundaries of the sampling areas were conventionally counted in or out depending on whether they lay across the S and W, or N and E edges respectively. Sampling of the gross size fraction had to be by coning and quartering as random sampling gave very erratic results in spite of the close size ratio (1.2). On the board, the total count was not permitted to fall below 1000 nor the total weight below 0.04 grams. W_s was always determined in duplicate and rechecked if good agreement was not obtained. Quartz (in the calibration) was counted on a board on which the counting areas were inked black.

(6) The accuracy of the counting operation is not as high as might be expected. Significantly higher accuracy could be attained only by more and more reduplication but the method is already cumbersome and tedious and further lengthening would hardly be justified by the increase in accuracy obtainable.

There is an inevitable sampling error due to the variance of the size, shape and density of the particles in a single size fraction. Even when the sieve size ratio was as low as 1.2 the weight ratio of particles of quartz was found to be of the order of 100. The variance of W_s in 5/6m. quartz was such that the accuracy of its determination from 1000 pieces was only ± 4.7°/o (95°/o level of probability), or ±3.3°/o if the average of duplicate determination was taken. A similar value was obtained for 14/16m. quartz. Quartz is however very irregular in shape any sample containing a wide range of shapes from needles to plates and it was not surprising to find that the corresponding accuracy obtained from the more uniformly shaped coke IV was ± 2°/o on the duplicate determination at 5/6m..

That error will probably not vary down to 52/60m. though mistakes in counting may tend to be more frequent at smaller sizes. When the counting board is used the error pattern is quite different. As the number of particles increases the error due to shape and size sampling rapidly becomes negligible and the major error is in the sampling of the population density of the board. An investigation of this error was made using 60/72m. Coke P. An error of ± 4°/o on the mean of the duplicate was obtained. This was done at rather an early stage and practice and improved technique may have reduced it later. This variance would probably be rather less at smaller sizes where the higher ratio of board or sampling patch area to particle projected area would improve the sampling of the population density. Certainly reasonably close duplicates (3°/o maximum difference) were normally obtained.

Apart from random errors in W_s such as those discussed above there have been encountered occasional values which, while readily reproducible lie wildly off the best line through the rest of the points. The only explanation of these anomalies that can be suggested is that they are a consequence of the rather erratic distributions obtained by sieving, already pointed out on page 55. They occurred in the calibration by quartz, and occasionally, occurring at or near an ogive in a coke curve have rendered the drawing of the best line rather difficult.

At the very smallest sizes it was already noted that in the calibration with Quartz and Coke P poor agreement was obtained. This suggests a falling off of reproducibility at these small sizes and while that is quite likely due to the difficulty of handling and weighing of small amounts of small particles, to the chance of contamination by dust at various stages, and to the rather less satisfactory sieving of these sizes, a completely new factor becomes of increasing importance - namely eyestrain. The extension of the counting to 300m. would have been desirable if 240 and 300 mesh sieves of sufficiently high accuracy had been available. (They were not being produced when this work was carried out). Improved counting methods would have had to be found however probably by making use of a binocular microscope of low power mounted over the counting board.

(7) The relationship between d_s and S can be determined only by microscope. Larger sizes of pores were examined on polished sections of coke with a binocular microscope. Smaller pores were examined in polished sections of particles of suitable size mounted either in Wood's metal or in diakon. A metallurgical microscope was used at suitably high magnification. Diakon was more convenient for mounting but sometimes the larger pieces were crushed and their pore structures destroyed during moulding.

Pore size was compared with particle size particularly at the uppermost and lowest ogive sizes. (It should be explained that two ranges of pore size were found and hence there are four ogives in the log W_s/ log S curve of each coke.) The size of the largest pores detected in any coke obviously corresponds with the particle size at the uppermost ogive. The largest pores found in particles of size corresponding to the lowest ogive were used to compare d_s and S at that size. It might be thought that the smallest should have been measured in this case, but there were always a very few minute pores detectable by microscope, so small and of such insignificant total volume that they were probably not included in the pore distribution. These "pores" may only have been small chords of much larger spheres, and it was thought justifiable to ignore them at this stage. Pores were examined at a few other sizes intermediate between the largest and smallest, and the information obtained has been summarized for all these experiments in Table VII.

TABLE VII. - Determination of the Ratio R = $^{d_s}/S$.

Coke	Particle Size S cms.	Pore Size d_s cms	$^{d_s}/S$ (R)	Method of Measurement
II	0.51	0.20	0.39	S from uppermost ogive of log W_s/ log S curve. d_s from largest pores on polished surfaces.
IV	0.51	0.23	0.45	
V	0.51	0.20	0.39	
VI	0.41	0.13	0.32	
VII	0.51	0.20	0.39	
P	1.90	0.91	0.48	
II	0.19	0.064	0.34	S from upper ogive of lower range. d_s from largest pores in 5/6m. coke.
V	0.038	0.018	0.47	Largest pores in 36/44m. coke.
I	0.023	0.0115	0.50	Largest pores in 60/72m.coke
P	0.061	0.025	0.41	S from lower ogive d_s from pores in 22/25m. coke.
I	0.0125	0.0038	0.31	S from lowest ogives. d_s from largest pore in particles of ogive size (about 100 - 120m.)
II	0.0125	0.0051	0.41	
IV	0.0115	0.0038	0.33	
V	0.014	0.0076	0.54	
VI	0.014	0.0025	0.18 *	
VII	0.016	0.0051	0.32	

* No explanation can be found for this very low value.

From the data in Table VII it can be deduced that the value of the ratio $R = d_s / S$ is approximately 0.4. This value cannot be determined precisely. It is thought that the average value obtained is probably rather low because it is more probable that d_s was measured low than high. Sampling was most inadequate, for only a small number of pieces of any coke could be examined - four or five of the large pieces or a few dozens of the smaller particles. Each of these pieces was examined in one section only which need not intersect the largest pore, or if it does will probably not do so diametrically. The probability of detecting the largest pore of all is therefore small but on the other hand an unusually large pore <u>may</u> be found of which there may be too few to be of any consequence.

For this reason the counting method cannot be expected to give pore size distribution in terms of <u>absolute pore size</u> but the distributions measured will probably be comparable from coke to coke. A complete cross-check on the method using an independent technique would be necessary if a more precise measure of pore sizes is to be made. The effect of the uncertainty in the value adopted for R, upon the pore surface areas and cell wall thicknesses deduced from the distributions will be indicated in the appropriate sections.

Criticisms of the method.

There are four possible causes by which the counting method may fail to indicate properly the variation in apparent density with size.

Firstly, the shape factor may change. This can be discussed only in the light of the results obtained and will be dealt with later in Section 12.

Secondly, diminution of porosity at broken surfaces may cause an increase in D_s at a size larger than that at which differential pore rupture occurs. The data obtained have been examined and there is no sign of this phenomenon having any effect. Some experiments were carried out on an agglomerate of lead shot (of known size analysis) in concrete, in which the shot was to represent pores and the concrete coke-carbon in an analogous "coke". The counts method was applied but failed to measure the "pore size distribution" because of "porosity" lost at the broken surfaces. In that case however the shot fell out rather readily, and the holes left behind were in effect "negative porosity of very high relative density" and the effect was very noticable indeed. But pores in coke can lose only a small fraction of their volume as they are exposed, the greater part of them being divided among the particles formed by the fracture.

A third possibility is that a similar diminution of porosity occurring at all particle sizes might distort the D_s curve so that there would appear to be a much lower porosity of small sizes than there really is. This point cannot be checked without finding a completely independent means of measuring pore size distribution, such as might have been afforded by the mercury penetration method. It may be remarked however that there has been found a surprisingly <u>high</u> proportion of porosity of very small size.

Fourthly, there is the possibility that in the comminution of the coke the more porous, softer and less (real) dense inner ends will break down faster than the hard dense cauliflower ends so that W_s for large sizes will be unduly high and that for small sizes too low. This point was successfully examined. At sizes as large as 5/6m. or $^3/16"$ - $^1/8"$ the values of W_s obtained from the small sizes screened out after the first breakdown and that from the larger sizes after the final crushing in the rolls were identical. At very small sizes no difference could be detected between the values of W_s from the normal sample and that obtained by crushing a sample as finely as possible in rolls. This possible source of error can be discounted.

Results.

The counting method has been applied to all seven cokes and the data are summarized in Figure 4 where log W_s is plotted against log S. The curve of Coke P is of the type predicted but the six metallurgical cokes show two "steps" apparently indicating two distinct ranges of pore size. The two ranges occur at similar sizes in all six cokes. The extent of the upper range is in each case very inadequately defined there being one point only in the middle of the "step" part of the curve.

The lower end of the range of small pores unfortunately corresponds with the smallest sieve sizes for which the values of W_s are determined with most difficulty, and for which calibration was least satisfactory. The drawing of this lower end of the curves has occasionally been difficult and it was for this reason that extension of the counting to 300m. would have been very useful.

The values of D_s have not been presented as they are not required in the calculation of pore size distribution and are of no interest in themselves.

The total displacement of the linear portion of the curves parallel to the log W_s axis is usually less than that calculated from the experimental values of D_a and D_r assuming constancy of k. It was this discrepancy which led to the development of the "diakon" method of measuring density, and the displacement calculated from D_a and D_d corresponds fairly well with that found by counting experiments. In other words the maximum values of D_s have been found to be approximately equal to D_d. The greatest difference between them was found in Coke V and amounted to about 6 per cent.

The interpretation of this is that the counting method measures the distribution of the bubble pores only. The question of the constancy of k is discussed in Section 12 and the calculation of the pore distribution is Section 13.

SECTION 11.

INTERMEDIATE DENSITIES (D_s) BY BULK DENSITIES (D_b)

An alternative method of tracing the changes in D_s with size is through the values of the bulk densities of closely sized material. This method was investigated for two reasons. Firstly, it was hoped that it would provide an easier alternative to the counting method, and secondly, that it might lead to a better understanding of shape factors.

The theory of the method is similar to that of the counting method. From geometric considerations the bulk density of a non-porous material would be expected to be independent of size but it will depend on apparent density, on shape, and on any factor affecting packing. Some of these factors are due to surface conditions like roughness, adsorbed layers as of moisture, and electrostatic forces. Others include air-cushioning between particles, the number of friction points in the bed, and the inertia of the particles. These last three vary in their effect, being much more important in small sizes, and as a result bulk density is generally lower with small material than with large.

Nevertheless Bulk Density may be expressed as

$$D_b = f. \quad p. \quad D_s$$

where f is a factor depending on shape, and the packing factor p depends on the various surface properties and mechanical effects already mentioned. D_s has the same significance as in Section 10, and is, of course constant for non-porous materials, or in coke size ranges of constant porosity.

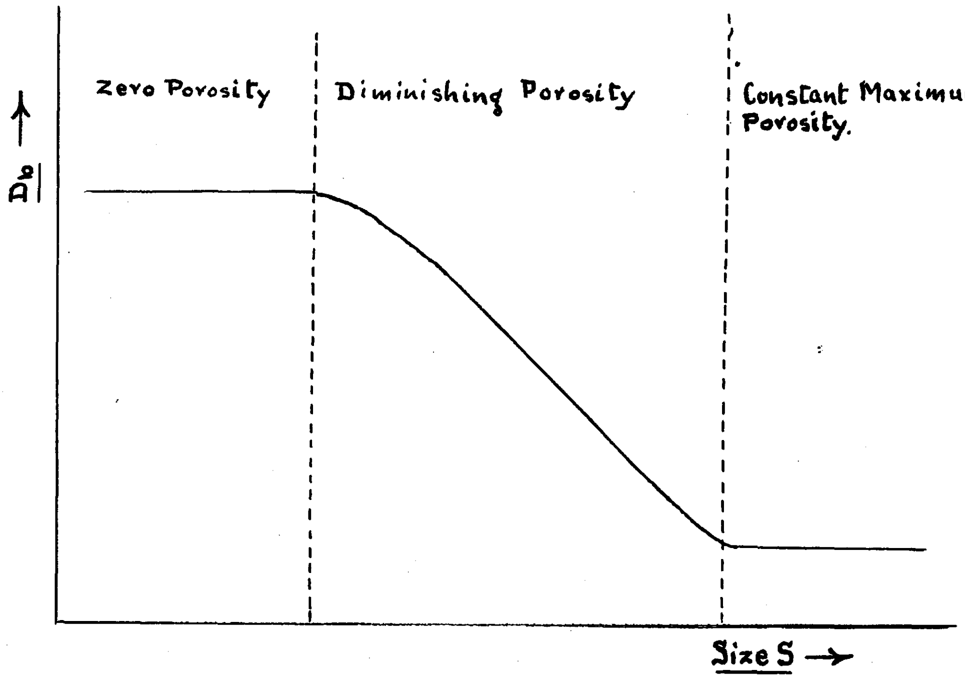


FIGURE 5. - Schematic Curve of Bulk Density v Size.

Then if D_b is plotted against S, the particles size, for a porous material like coke in which the value of D_s increases from D_a to D_r over a certain size range, a curve like that in Figure 5 will be obtained. If f and p are constant the ratio of the maximum to the minimum value of D_b would be expected equal to D_r/D_a, and that of any intermediate value of D_b to the minimum equal to D_s/D_a

Very little appears in the literature on the effect of size on the shape or packing factors relating to bulk density. Indeed very little has been published on closely sized material at all except theoretical considerations on the packing of spheres. Roller (26) has published some data showing a large increase in voidage of sized materials below 20μ (200m. is 76 μ). Gypsum, portland cement and anhydrite behaved similarly with voidages of 43-45$^{o}/_{o}$ at larger sizes while the smallest voidage given by chrome yellow was 55$^{o}/_{o}$. The difference may be due to shape but the condition of Roller's materials is not known. Below 20μ the sudden increase in voidage was probably due to one or more of the factors affecting packing becoming of increasing importance at diminishing size. The only other information found is summarized from Dallavalle (25) in Table VIII

TABLE VIII. Voidages found in Various Packed Materials.

Material 16/38m.Tyler	Voids $^{o}/_{o}$ of Total Volume
Spherical Pb Shot	37.18
Spherical S Shot	37.35
Dune Sand	37.60
Beach Sand	36.55
Marine Sand	34.78
Crushed Quartz	41.2
Crushed Calcite	40.76
Crushed Halite	43.51
Mica	86.62

The materials were sized in the rather wide range 16/38m. Tyler, (Size ratio = 2), and this probably accounts for the much smaller voidages than are obtained in this work. Table VIII demonstrates clearly the dependency of voidage upon shape. Spheres gave values about 37 $^{o}/_{o}$; oblique spheres lower, about 35$^{o}/_{o}$; and angular particles something over 40$^{o}/_{o}$. Closer sizing would increase these all round. In the present work with a size ratio of 1.2 the voidage of crushed quartz was never less than 47$^{o}/_{o}$ and that of large coke about 41 - 47$^{o}/_{o}$. These figures were found to increase between 51 and 55$^{o}/_{o}$ for coke at the smallest sizes.

The measurements of D_b is very simple. There are two possibilities - loose packing and closest packing. The latter is by far the more reproducible. Coke was sized as for the counting method but rather more of each fraction was required. Each size was coned carefully and poured into a measuring cylinder of suitable dimensions. This had to be at least 8 times the diameter of the particles and had to be filled to a height at least 6 times the diameter of the cylinder (26). The cylinder was tapped until the level of the coke could not be made to fall any further. The volume it occupied in the cylinder was then noted and it was poured out and weighed, D_b was then simply the ratio of the mass to the measured volume.

When the size was below 44m. the cylinder was evacuated during the packing process. This speeded up packing of the coarser of these fractions and rendered close packing of the finest fractions possible as air cushioning between the particles seems to contribute toward the poor packing normally met with in fine powders.

The accuracy of the determined bulk density depends on the reproducibility of the volume measurement. High values are generally more acceptable than low ones because it is a <u>maximum</u> packing density that is being measured. Sieving and sampling errors are small but packing appears to depend on how the sample had been mixed. Coning of the sample before pouring into the cylinder was adopted as standard procedure because it improved reproducibility. Duplicates within 2°/o were generally obtained. The necessity of employing larger size ratios than the 1.2 of the B.S.S. sieves in the larger sizes led to the effect of size ratio on bulk density being investigated. Between the standard value of 1.2 and about 1.5 the effect was negligibly small. This range covers the requirements of this work.

The bulk density of quartz was determined to find how it varied with size as a guide to what might be expected of coke. The results are plotted in Figure 6 along with those of cokes VII and P. They are erratic but show a marked fall in bulk density with size. On the other hand the bulk density of Coke P in its range of zero porosity below 25m. is remarkably constant, corresponding to a voidage of 52°/o that is the same as that of small quartz. The erratic values obtained of quartz may be due simply to its very wide range of shapes to which was attributed in Section 10 the large variance of its value of average particle weight W_s.

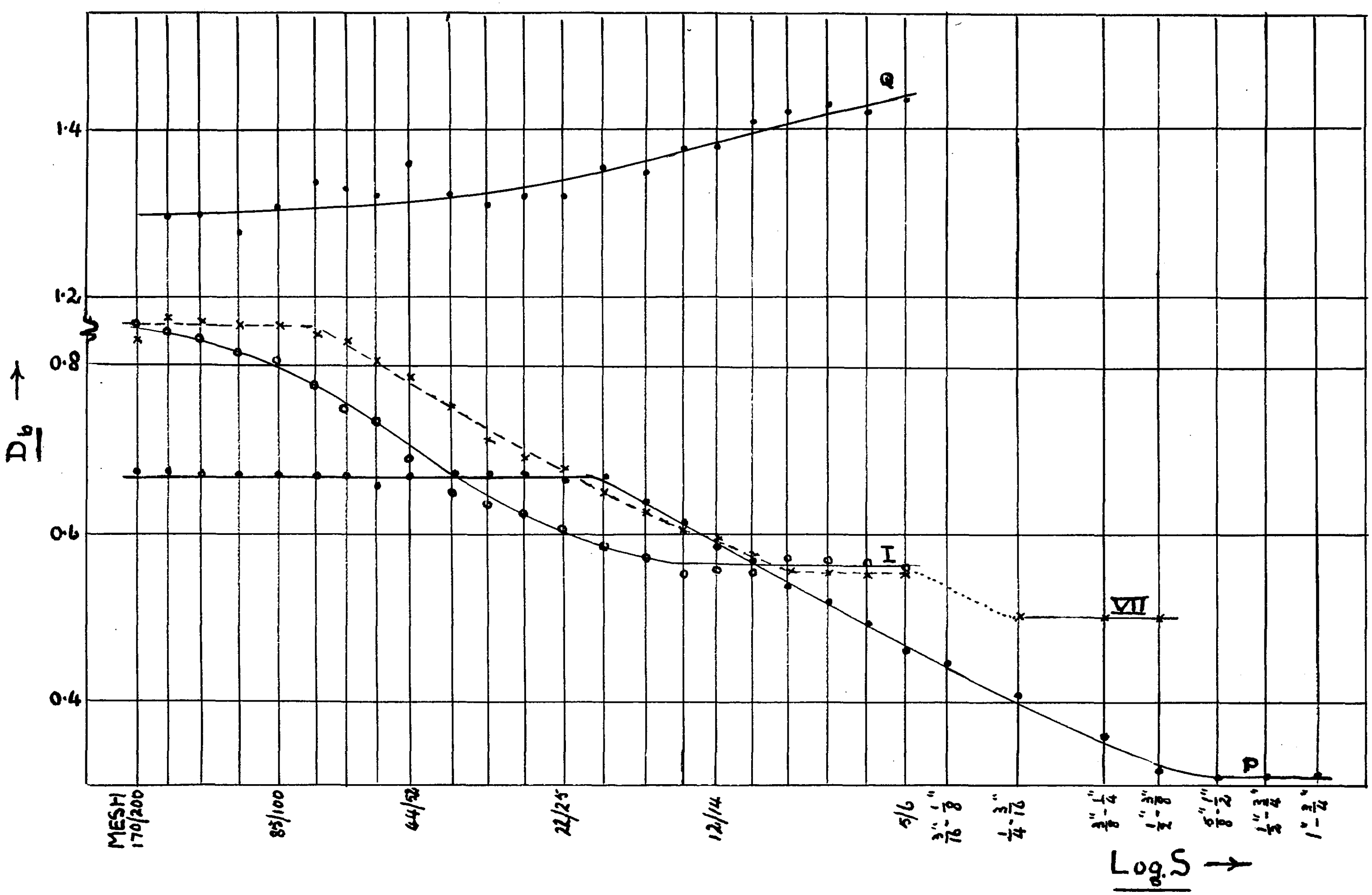


FIGURE 6. - Variations of Bulk Densities of I, VII, P and Q with Size.

The fall in bulk density of quartz does seem to be real however. It occurs mainly in sizes above 22m.. Below that size bulk density may be considered almost constant but very erratic. The cause of the fall cannot be explained especially as the (counting) shape factor k was constant.

Bulk densities of cokes I, VII, and P were determined at all mesh sizes and VII and P at some larger sizes also. The other cokes were determined at small and large mesh sizes and at a few larger sizes, interest having focussed on the size ranges of constant porosity. Data for cokes I, VII, and P are summarized graphically in Figure 6 where D_b is plotted against S . The curves are of the expected form. Coke VII shows the double step indicating the two ranges of pore size as did the counting method. Coke P had one pore size range only as expected. Data at large sizes were not obtainable for Coke I. Curves for the other cokes were in line with those of I and VII and are not presented as they add nothing of value at this stage. The data pertaining to the largest sizes only have been included in Table III for another purpose.

Broadly speaking the "steps" obtained indicate the same pore ranges as were obtained from the counting method but with differences in details. Ogives are generally less sharp and the lower pore ranges rather wider than by the counting method. The value of D_r/D_a is invariably much lower than that obtained from density measurements of from the counting method. This conforms with the behaviour of quartz and must be due to some change in properties affecting packing. This question is discussed in full in Section 12 along with other relevant information in a general consideration of the properties of particulate matter.

On the whole these experiments have contributed little to the understanding of shape factors and show no sign of being useful as an alternative to the counting method for estimating pore size distribution because of the change in packing characteristics in a size range which cannot be determined exactly. This is particularly unfortunate since the technique has been found to be so simple and reproducibility reasonably good.

PART FOUR.

CONCLUSIONS.

SECTION 12.

SHAPE FACTORS.

Total ignorance of shape factors was a matter for some concern when the work was commenced. Something has been learned on the way, but the information obtained is limited to a few materials only and even among these some features lack explanation.

The shape factors k obtained by the counting method are given in Table IX. Two values are given for each material - the constant value for large pieces which had lost no porosity, and that for small particles which were free of pores. Alongside are given the voidages applying to the bulk density measurements - again two values for each material. The values of k were of course obtained from the log W_s/ log S graphs, from the intercepts in the ordinate log $S = 0$ ($S = 1$cm.) of the linear parts of the curves (produced if necessary.). The intercepts give the values of log (k.D) whence k can be obtained if D is known. D is either D_a or D_d, and the accuracy of k cannot be better than that of the appropriate density value. The accuracy of the Voidage figures is probably not better than $\pm 3^o/_o$ as they depend on D also, and on the bulk density determination.

An important feature of the log W/log S plots is that the gradients of the linear portions are all very close to 3 . This applies to the very large sizes of porous cokes; to the intermediate sizes in which there is apparently no pore rupture; to the small sizes where the cokes are non-porous; and particularly to quartz and the non-porous range of sizes of Coke P.

It would seem that an earlier assumption that values of k vary little with size is probably justified for materials of constant or zero porosity. The assumption is still subject to the nature of the material however and may not hold for those with strong directional cleavage such as coal or mica.

TABLE IX. - Shape Factors and Voidages.

Coke	Shape Factor k		Voidage %	
	Large	Small	Large	Small
I	0.604	0.618	-	53.1
II	0.589	0.557	43.0	55.0
IV	0.635	0.619	41.4	54.5
V	0.656	0.638	41.6	51.7
VI	0.650	0.628	43.7	53.0
VII	0.640	0.618	43.7	53.3.
P	0.650	0.626	43.5	52.0
Q	0.642	0.642	46.3	51.0

The general impression gained from Table IX is that shape factors have a rather limited range of possible values but within that range the variation appears quite random. Coke II for example is a blocky coke for which a high factor might have been expected, but it has the lowest factor; P on the other hand is a soft material forming rounded lumps for which a low value of k approaching that for spheres would have been predicted, but its value is one of the highest. Then even where there is a change in porosity the change in k within this limited range will probably be small. The assumption that k would be nearly constant even for non-porous materials is therefore justified.

The difference between the values of k for large and small sizes of the same coke is of course a measure of the accuracy with which the counting method has measured its porosity. The abvious tendency for k to have a smaller value at smaller sizes cannot be explained.

....

The voidage figures (Table IX) are of little use in helping to interpret the variations in k . They too vary within a narrow range but in a random fashion that is apparently quite unrelated to the variations in k . The voidages obtained at large sizes correspond fairly well with those given in Table VIII for crushed materials - especially considering that the size ratio is in this case much smaller (1.2 against 2.0). These are being considered "normal" voidages and those obtained at smaller sizes are being considered "high". Most of the bulk densities measured have therefore been "low" for reasons that will be discussed later.

The differences between the voidages of the large and small sizes of the cokes has been found very large and this corresponds to a big error if porosity is being estimated from bulk density data. This alone is sufficient reason that pore distribution should not be measured by that method.

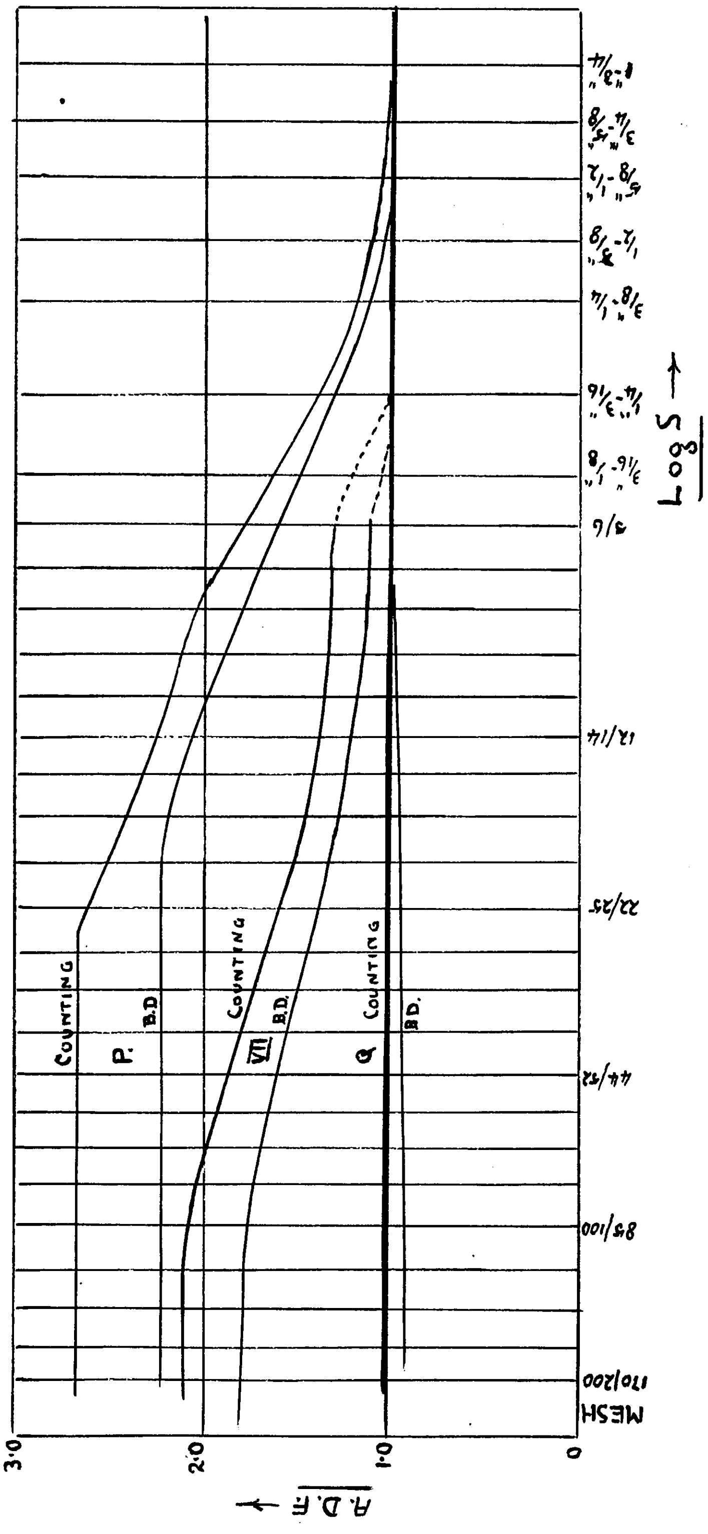


FIGURE 7. - Variation in Apparent Density Factors with Size by Counting and Bulk Density Methods.

Figure 7 has been prepared to show how the Apparent Density Factors ($^{D}s/_{D_a}$) measured by the two methods differ. The graphs have been drawn for Cokes VII and P and for Quartz. Coke VII is typical of the metallurgical cokes and was chosen because its data were most complete. In that case the results by the two methods diverge most markedly at large sizes, the difference established at 5/6m. being maintained with only slight increase down to about 60m.. At still smaller sizes the factor by bulk density fell still lower than that by counting. The bulk density at very small sizes was not quite constant but continued to increase slightly although the counting method indicated no pore rupture. Coke P again showed the factors to diverge rapidly at large sizes and the difference then became practically constant between 6m. and 16m. but again increased rapidly for the counting method indicated pore rupture to 22m. size, while the bulk density was constant below 16m.. In this case voidage and k were both constant over a very wide range of sizes down to 200m.. Quartz, being non-porous and having a constant k would have been expected to behave in this way too, but its apparent density factor by bulk density is shown to have diminished (rather erratically) with diminishing size. (See also Fig 6.)

It might be deduced that the increase in voidage obtained of quartz is a normal function of size liable to be found in all materials to a greater or less degree. Coke P however is a very notable exception which prevents a general conclusion being drawn.

The reason for the apparent changes in packing characteristics are rather difficult to determine with certainty, and little can be added to the brief review in Section 11. In the first place it is being assumed that as the shape factor with respect to W_s is constant (or nearly so), that referring to bulk density will be constant too. But even this is not certain. Packing is, however subject to other factors than simple shape, and surface roughness is probably the most important in the case of porous material like coke. When its particle size is decreased so far that the features of the surface which make it "rough", that is the exposed pores, are of size comparable with the particles themselves then it may be expected that the particles will pack differently. The part which may be played by projections from the main body of the particle in holding it apart from others can be imagined qualitatively but could hardly be subjected to measurement. ? A strong effect due roughness would be expected down to the smallest sizes in which there were pores but might at small sizes be augmented by other factors such as adsorbed films, electro-static effects, or, probably most important, greatly increased friction effects due to the rapidly increasing number of points of contact throughout the bed of coke. At each of these points the energy required to shake the particles into their most compact arrangement would tend to be dissipated as heat, and as their number increases it becomes more and more difficult to transmit vibrations through the bed. The highest values of bulk density then obtained would fall short of the theoretical maximum values. Thus "low" bulk densities obtained at large sizes such as 5/6m. are probably due to surface roughness effects; those at small sizes are more likely to be caused by other factors such as described above.

As the greatest increase in voidage in the metallurgical cokes occurred near the size range in which the largest pores are broken down, it would be interesting to know if the change in k also occurs in this same range. If this could be proved it would be a valuable contribution to reducing the uncertainties of the counting method for pore distribution. Unfortunately there is no way of applying the small amount of data available to prove or disprove this point.

SECTION 13.

THE PORE SIZE DISTRIBUTION OF COKE.

In this Section the calculation of the pore size distribution from the counting data is described and the results obtained are presented along with some explanations and criticisms.

Only the distribution of "bubble" pores defined in Section 7 has been measured and the values of "bubble" porosity given in Table VI have been employed in the calculation. An alternative value can be deduced from the counting data assuming a constant value of k . The porosities obtained by the two methods are listed for comparison in Table X. Each method is liable to its own errors and there is a small fundamental difference between the quantities that they measure. Bubble porosity is defined by D_a and D_d whereas the counting method gives the porosity defined by D_a and D_s where S corresponds to the aperture size at the lowest ogive. The difference between D_s and D_d is due to the surface concavities in these

TABLE X. - Porosities by Densities and by Counting.

Coke	I	II	IV	V	VI	VII	P'
Bubble porosity by densities%	51.5	59.1	51.1	50.5	47.1	51.5	61.2
Bubble porosity by counting%	52.7	57.2	49.6	47.5	45.0	49.9	59.7
% Error.	2.4	3.2	2.9	6.0	4.5	3.3	2.4

small particles the volume of which was originally pore volume. Diakon fills these pores but in the counting method their volume is reckoned as pore volume. Porosities by the counting method are therefore lower than those by densities. The latter are more correct and have been accepted as the bubble porosities of the cokes.

The next question is how to deal with the changing value of k . As there is no means of attributing the change to any particular size or size range it has been decided to regard the error as being distributed proportionately over all sizes . The chief justification for this assumption is its simplicity. It has the advantages of ease of operation and that the attendant error is spread over the widest range of sizes thus minimizing its effect.

The Calculation

The method of calculating the pore size distribution curve can best be described by working through a specific example. The data of Coke I will be used.

From the log W_s/log S plot already presented in Figure 4 (in back pocket) the value of the "Apparent Density Factor" (A.D.F.) corresponding to each size plotted was abstracted. This factor is the ratio D_s/D_a and is obtained as the antilogarithm of the intercept on the ordinate at S between the curve plotted and the straight line part of it corresponding to maximum porosity, produced to size S . The necessary construction has already been indicated in Figure 2.

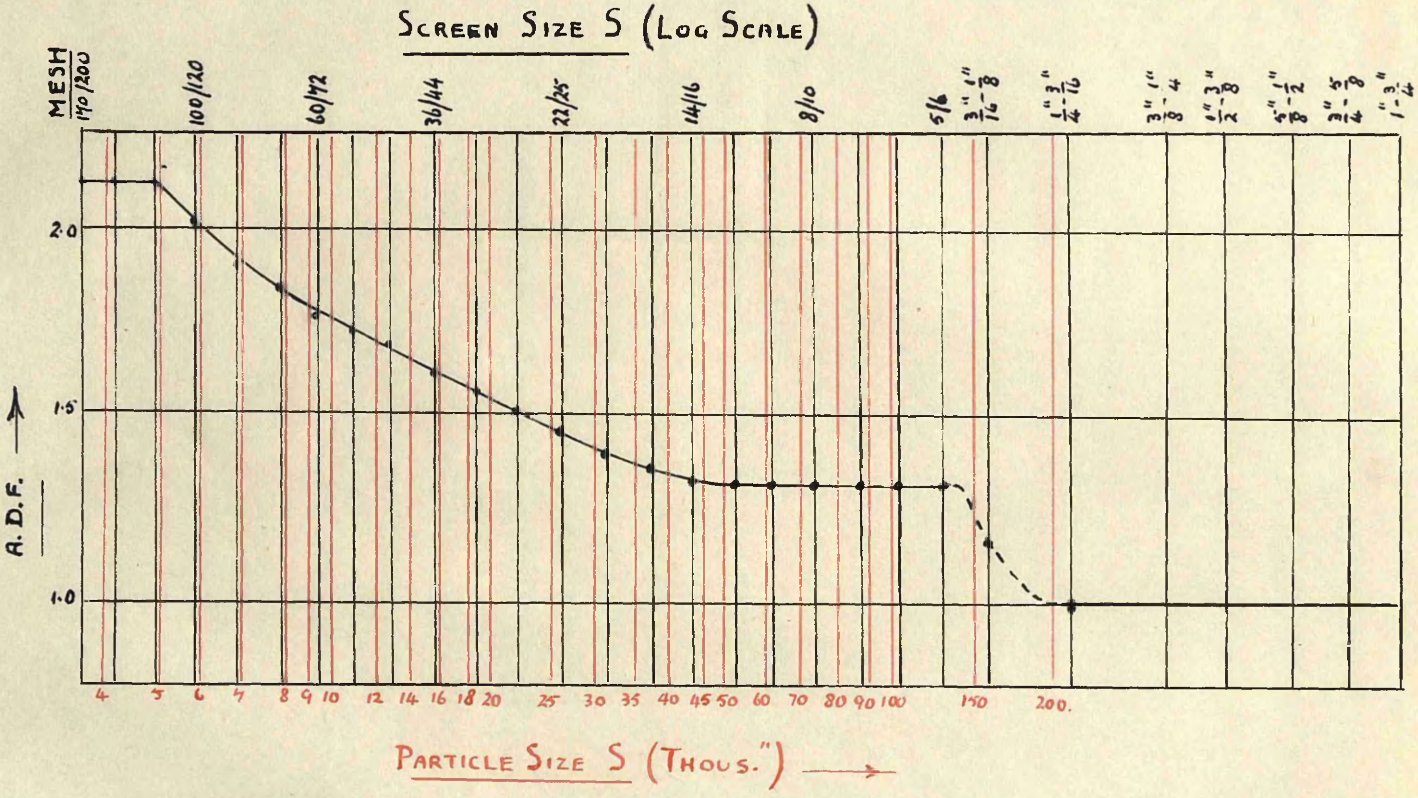


FIGURE 8. - Apparent Density Factor of Coke I plotted against (log) Size to "Smooth" data and to show how Size is transformed from "Mesh" to Thousandths of an inch.

These Apparent Density Factors were plotted against log S as in Figure 8 where their values were "smoothed" and then read off against the more convenient set of sizes , in the scale of thousandths of an inch. These values are listed in Table XI where the rest of the calculation was carried out.

In Column I of Table XI are listed the values of size chosen. They are all in thousandths of an inch.

Column 2 gives the corresponding values of the A.D.F. read off Figure 8 (on a larger scale).

In Column 3 are calculated the values of $P_s = 1 - D_a/D_s$ which is the porosity destroyed by degradation to size S , and is being considered as composed of the pores larger than 0.4 S in diameter. (see page 65.)

The maximum porosity given in Column 3 is the value obtained by the counting method and listed in Table X.

In Column 4 all porosities have been reduced proportionately so that the maximum porosity is that calculated from densities D_a and D_d. This adjusts the data to the basis of constant shape factor.

In Columns 5 and 6 the cumulative distribution data of Column 4 are differentiated with respect to size. The increment of porosity corresponding to each size range is listed against the mean value of S in that range.

It will be noted that all of these size ranges are not of equal width and in Column 7 the increments of porosity have been adjusted by the necessary factor to be per cent of porosity per 1/1000th of an inch in size range.

TABLE XI. - Calculation of Pore Size Distribution.

1	2	3	4	5	6	7	8
Particle Size (Thous")	A.D.F.	Porosity >0.4S	Porosity >0.4S (corrected)	Mean of Size Range S.	Porosity corresponding to Size Range at S.	Porosity per Thou" Range	P/S. (6/5)
200	1.00	0.0	0.0	150	25	.25	0.167
150	1.19	16.0	15.6				
100	1.343	25.6	25.0				
44	1.343	25.6	25.0	43	0.2	0.1	0.0046
42	1.348	25.8	25.2	41	0.3	0.15	0.0073
40	1.354	26.1	25.5	39	0.6	0.3	0.0154
38	1.363	26.7	26.1	37	0.7	0.35	0.0191
36	1.378	27.4	26.8	35	0.6	0.3	0.0172
34	1.390	28.0	27.4	33	0.85	0.43	0.0257
32	1.405	28.9	28.25	31	0.9	0.45	0.0290
30	1.428	30.0	29.35	29	0.85	0.44	0.0292
28	1.449	30.9	30.2	27	1.1	0.55	0.0410
26	1.470	32.0	31.3	25	0.9	0.44	0.0360
24	1.490	32.9	32.2	23	1.2	0.6	0.0522
22	1.520	34.2	33.4	21	1.35	0.68	0.0622
20	1.550	35.5	34.75	19.5	0.45	0.45	0.0231
19	1.562	36.0	35.2	18.5	0.6	0.6	0.0324
18	1.578	36.6	35.8	17.5	0.8	0.86	0.0456
17	1.593	37.3	36.5	16.5	0.7	0.7	0.0424
16	1.611	38.0	37.2	15.5	0.8	0.8	0.0515
15	1.632	38.8	38.0	14.5	0.7	0.7	0.0482
14	1.658	39.6	38.7	13.5	0.9	0.9	0.0678
13	1.680	40.5	39.6	12.5	0.65	0.65	0.0520
12	1.700	41.2	40.25	11.5	0.75	0.75	0.0652
11	1.725	42.0	41.0	10.5	0.9	0.9	0.0858
10	1.751	42.9	41.9	9.75	0.6	1.2	0.0616
9.5	1.770	43.5	42.5	9.25	0.7	1.4	0.0754
9.0	1.790	44.2	43.2	8.75	0.55	1.1	0.0629
8.5	1.808	44.75	43.75	8.25	0.6	1.2	0.0728
8.0	1.830	45.4	44.35	7.75	0.65	1.3	0.0863
7.5	1.855	46.1	45.1	7.25	0.9	1.8	0.1240
7.0	1.890	47.1	46.0	6.75	1.45	2.9	0.2150
6.5	1.940	48.5	47.45	6.25	1.3	2.6	0.2080
6.0	1.992	49.9	48.75	5.75	1.3	2.6	0.2260
5.5	2.050	51.3	50.05	5.25	1.25	2.5	0.2190
5.0	2.105	52.5	51.2	4.75	0.15	0.3	0.0350
4.5	2.115	52.7	51.5	4.25	0.0	0.0	0.0
4.0	2.115						

Sum of Column 8 = 2.407

At this stage comparative distribution curves could have been drawn but it was found desirable first to smooth the data again by plotting the values in Column 7 against log S as in Figure 9 and to extract therefrom suitable figures for replotting on an arithmetic basis. These figures were adjusted in several respects. Firstly values of S were converted to pore diameters d_s, and ~~then~~ from thousands of an inch to millimetres, using the factor 0.01. Secondly values of porosity increment were converted to per cent porosity per 1/100mm. range of pore sizes.

The distribution curves presented in Figure 10 were then drawn. The form of the curve for the upper range could not be calculated on the data available. The curves drawn indicate only the size range of these larger pores and their contribution to the porosity is noted in each case. No attempt has been made to represent the intermicellar porosity in these diagrams.

The distributions for Cokes I, II, IV, V, VI, and VII are all drawn to the same scale. The ordinate at any pore size d_s is proportional to the <u>volume</u> of pores of that diameter. The areas under the curves are proportional to the total bubble porosities. The distribution for Coke P has been drawn to different scales and cannot readily be compared with the others. Distributions by numbers of pores rather than by their volume appear similar in form but with the mode at the small sizes greatly exaggerated and the contribution of porosity by larger pores apparently greatly diminished.

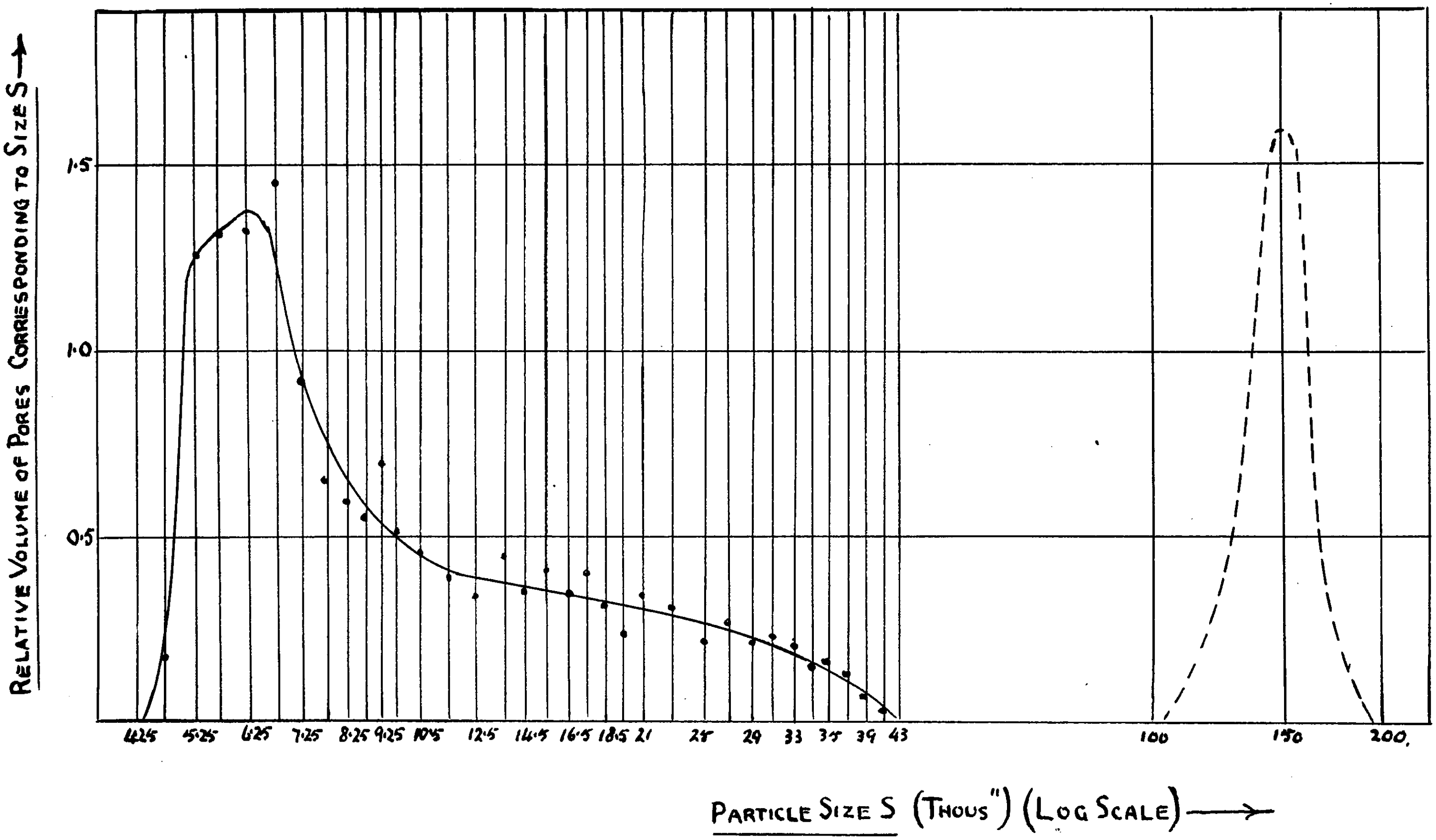


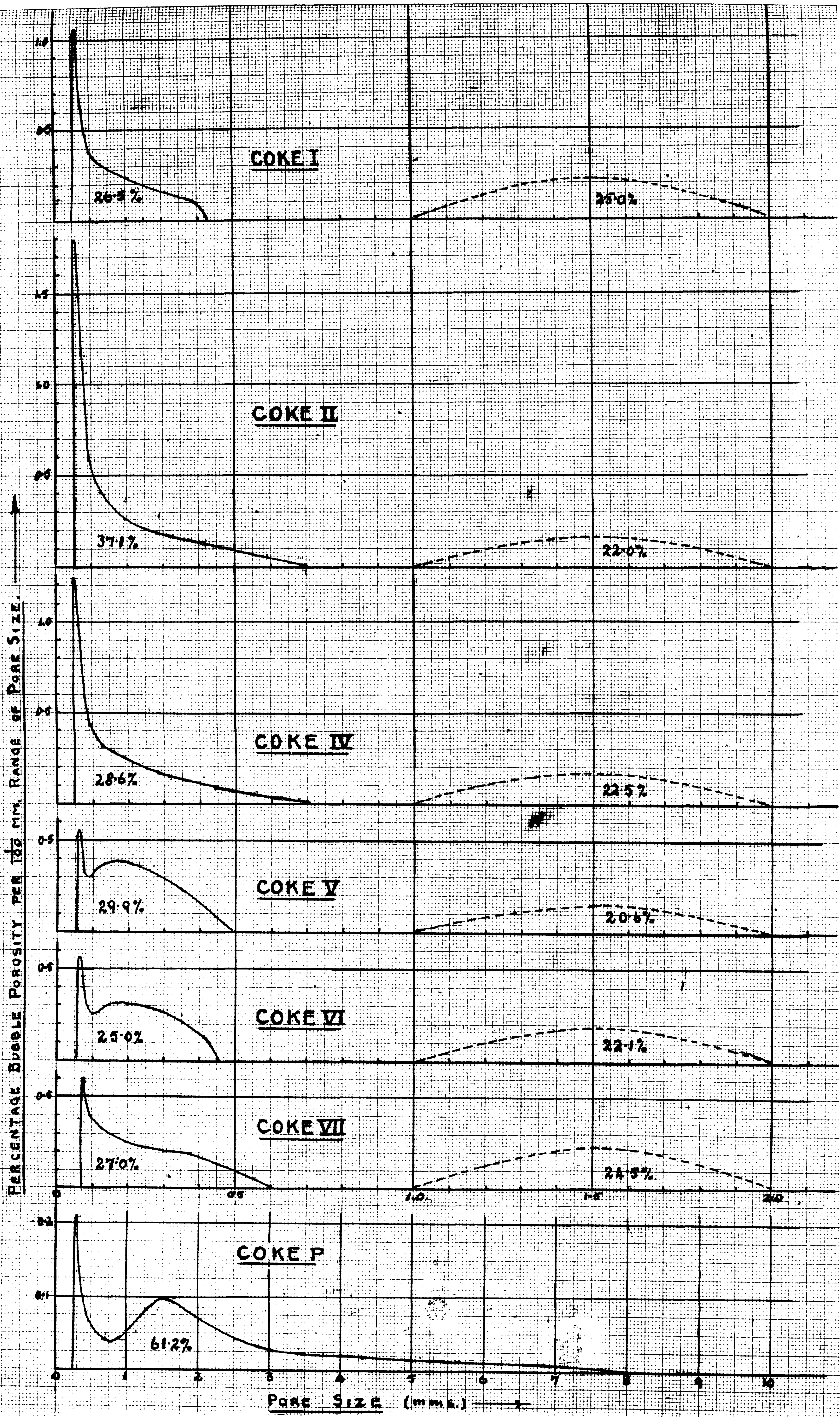
FIGURE 9. - Pore distribution of Coke I plotted to base of Log S. "Smoothed" data are then transferred to Fig. 10 with adjustment of units.

This distribution is very difficult to present graphically but it was calculated that there are some thousands of pores of sizes in the lower range for every one in the upper range. It is surprising to find that this ratio is so high. It has not been possible to devise an independent check on this work and the distributions are accepted as substantially correct and are discussed below.

Comments.

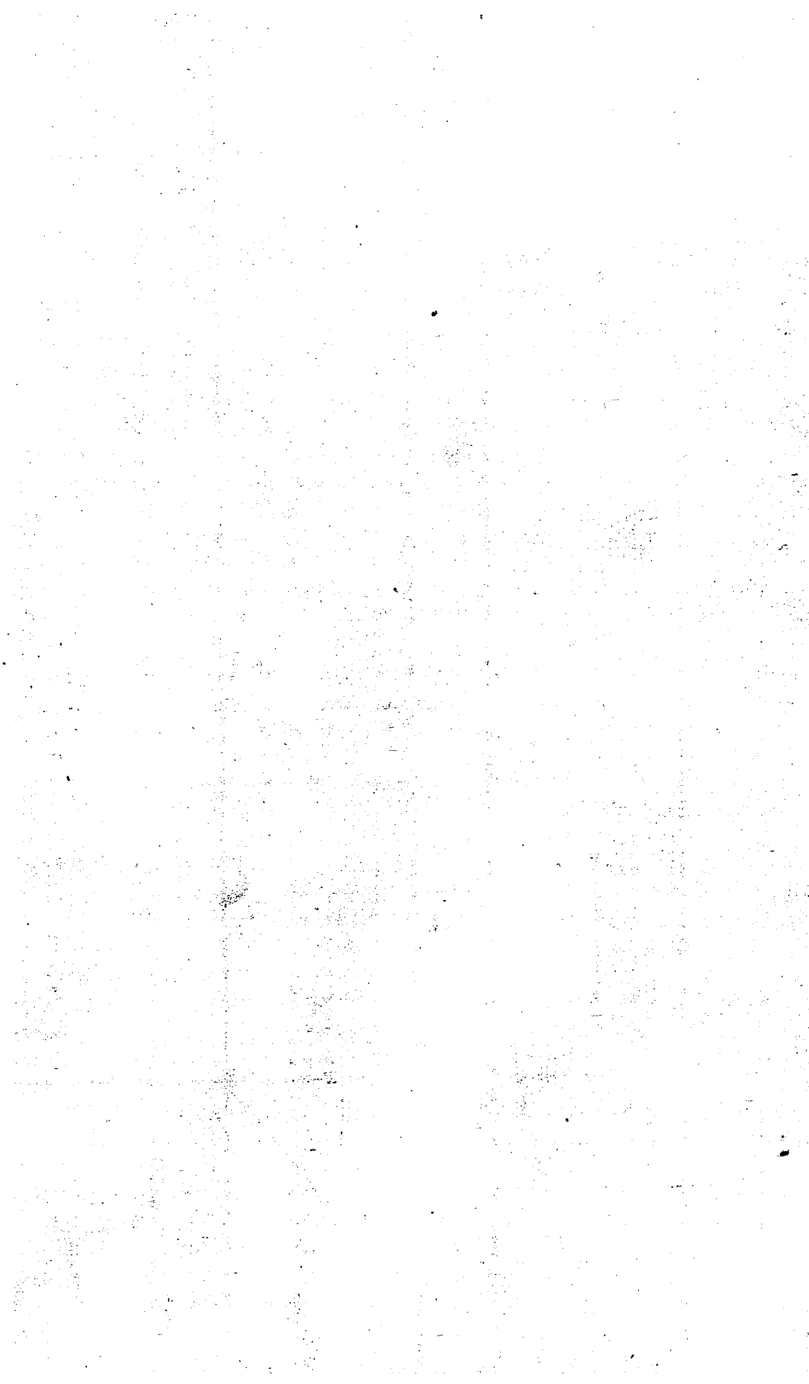
The most surprising feature of the pore size distributions of the six metallurgical cokes is their distinct division into ranges. Apart from the range of intermicellar pore sizes the bubble pores are divided into two ranges, the lower between 0.05mm. and 0.7mm. and the upper from about 1mm. to 2mm. with apparently a range of sizes between, of which there are no pores. Each range accounts for approximately half the porosity in every case.

The upper and lower limits of each range are quite similar in all six cokes although the uncertainty in the largest sizes may be as great as 0.25mm.. It is probably much less however, and in any case would have little effect on the values of pore surface areas and cell wall thicknesses calculated later. The evidence is clear that insofar as "visible" sizes of pores are concerned there is no important difference between any two of these cokes. It must be stressed that it is the average pore structure that is being considered and that much larger pores than measured are almost certainly present in all of the cokes but in such small proportions as



PORE SIZE DISTRIBUTIONS IN THE VARIOUS COKES EXAMINED

Figure 10.



not to be detectable by the present methods. It can probably be assumed that such pores make a negligible contribution to the properties of the coke. They will mainly be present at the soft inner ends which are most easily abraded and are probably broken down to breeze sizes before the coke reaches the de-breezing screens.

Examining the forms of the distribution curves of the lower size ranges it will be noted that there are two types of curve. Cokes I, II, IV and (perhaps) VII give unimodal distributions with very prominent modes at 0.06mm., 0.055mm., 0.05mm., and 0.075mm. respectively. The mode of VII was less pronounced than the others, and in this and certain other respects it falls rather into the other type with V and VI whose distributions in this range were bi-modal, with a weak mode at about 0.06mm. in each case and another wide, lower maximum at about 0.2mm..

The general form of the distribution curves could not have been predicted by microscopic examination. A pronounced mode was suspected, however among the largest sizes and its presence has been confirmed in the upper range of sizes. The marked break in the curve between the upper and lower size ranges is quite unexpected and subsequent microscopic examination fails to convince that such a wide range of pore sizes is definitely missing. It may be that there is only a very distinct minimum in the curve and that the counting method is not sufficiently sensitive to record the small amount of porosity in the range. Another possible explanation is suggested in a footnote to this section. This particular feature of the distributions is in any case very significant occurring as it does in all six metallurgical cokes, though <u>not</u> in the paraffin coke.

There are two possible explanations of this separation of pores into two size ranges. They are not incompatible but rather tend to reinforce each other, and may both operate.

There was mentioned on **p. 17** the possibility that pores may form within coal particles in the early stages of carbonization, or from the interstices between them as softening and coalescence proceeds. There is a strong suggestion that the pores in the lower range of sizes are formed within the coal particles and the bigger pores in the voids between them. This is supported by observations made under binocular microscop that while the small pores are nearly always spherical, larger ones are frequently irregular, frequently burst one into another and to some extent ramifying.

The other explanation is that in analogy with, say, soap bubbles the excess pressure in a small pore during intumescence will be much greater than that in a large pore, so that large pores will tend to grow at the expense of small ones, provided they are connected and as long as the carbonizing material is sufficiently plastic to flow. It seems doubtful if this mechanism alone could bring about the type of distribution found but it could make a contribution once a pore size differential had been set up by the first mechanism suggested.

If these suggestions are accepted, it follows that the smallest pores are connected with the larger pores, either not at all, or only through passages offering very high resistance to gas flow otherwise they would have been destroyed while the coal was still plastic. Small pores make a very big contribution to pore surface area but if the above is true that contribution must be largely inavailable for combustion.

The distributions obtained of the lower range of pore sizes are particularly interesting because the differences between them constitute one of the most distinctive features differentiating the cokes. While the possible effects of these differences will be discussed in the next two Sections, it will be mentioned here that an investigation of their <u>causes</u> might lead to important information on the mechanism of coking in the temperature range in which these smallest pores are formed. The reason for the formation of such very large numbers of very small bubbles in say Coke II compared with Coke VI must depend on the physical characteristics of the coals from which they are made. The present work was not designed to enquire into this problem and the necessary information on the coals used was not collected so that further discussion on <u>these</u> coals could only be speculative.

The distribution of pores obtained for Coke P is much wider than those of the metallurgical cokes. It is bi-modal rather like the lower range of V and VI. The distribution shows no unexpected or unexplainable features except that the reason for the lower mode is not clear. It has not been explained for the other cokes either however, but is probably a function of gas evolution rate and permeability to gases of the carbonizing material. An important feature is that there is no complete separation of the pore sizes into two distinct ranges. Such a distribution could not have been explained for Coke P in the same way as it was for the metallurgical cokes because paraffin coke is made from oil residues having no interstitial voids from which the large pores might have been formed.

The qualitative descriptions of these distributions are interesting and have led to some useful speculation but their real value lies in any quantitative derivations which can be made from them. When the calculations of pore surface areas and cell wall thicknesses have been made and discussed in the subsequent sections the real differences between the distributions will be come evident.

Footnote.

A note should be added here on a possible reason for the surprisingly distinct gap in the distributions. If the larger pores are formed as suggested from the voids between the coal particles, and if these larger pores are joined and ramifying, they may form a network of weaknesses, one effect of which would be that their presence in particles below a certain size would be improbable, for they would render such particles so weak that they would break to smaller sizes. Thus it can be imagined that the relationship

$$d_S \doteq 0.4S$$

might break down within a restricted range of d_s and cause some error in the determination of pore size distribution. This can only be a tentative suggestion, but the idea might be worthy of further investigation. It might lead to information on the formation of shrinkage cracks and incipient fissures in coke, factors of great importance affecting strength.

SECTION 14.

PORE SURFACE AREAS.

Pore surface area may be calculated as follows from the pore size distributions if the assumption is made that the pores are spherical. Microscopic examination shows that this is approximately true for the smaller pores, that is those in the lower range, but that the surfaces of the larger pores are more irregular. As these contribute only a small proportion (about 10°/o) of the total surface area the error involved in making the assumption is not high, and as the volume of large pores is similar in all cokes it seems reasonable that the magnitude of the error will not be very different from one coke to another. The ordering of the cokes should not be affected.

Considering the pores in a narrow range of sizes of diameter d let their volume v be a fraction p of the total pore volume, i.e. $p \cdot P$ of the coke volume where P is the fractional porosity of the coke.

The Volume of each pore $= \frac{\pi}{6} d^3$

The Number of Pores per unit Coke volume $= \frac{6pP}{\pi d^3}$

The Surface area of these pores $= \frac{6pP}{d}$

Therefore the total pore area per unit coke volume $= \sum_d 6\frac{pP}{d} = 6P\sum_d \frac{p}{d}$

The evaluation of $\sum_d \frac{p}{d}$ is most readily demonstrated by extending Table XI. The values in Column 5 are proportional to d, being greater by a factor $1/R = 1/0.4$ in every case. Values in Column 6 are proportional to p and as their sum equals 100 P each, divided by 100 P gives the fractional porosity p that is required. Column 8 gives the quotients of the values in Column 6 divided by those in 5 and their sum multiplied by $\frac{1}{0\cdot4 \times 100P}$ is the required $\sum_d \frac{p}{d}$

Hence the pore area per unit volume of coke is obtained as (the Sum of Column 8,X $\frac{6}{40}$). The units must still be adjusted to cm^2/cm^3 .

The values obtained for the various cokes are given in Table XII, along with those of cell wall thickness. These values are dependent on the validity of the factor $R = 0\cdot4$, any error in which causes an inversely proportionate error in the pore area.

TABLE XII. - Pore Surface Areas and Cell Wall Thicknesses of the Cokes Examined.

Coke.	Pore Surface Area in $cm.^2$ per $cm.^3$ of Massive Coke.	Cell Wall Thickness in mms..
I	142	0.058
II	185	0.045
IV	152	0.055
V	114	0.082
VI	99	0.091
VII	99	0.087
P	31	0.25

Coke P is out of line with the others for obvious reasons and need not be considered further.

Among the metallurgical cokes it is at once apparent that the Scottish Cokes I, II, and IV have a much more extensive pore surface than the Durham and Welsh cokes. This can be attributed largely to the pronounced maxima in their distribution curves at about 0.07mm.. That is particularly noticable in II which has by far the greatest surface area. The contributions made by various size ranges of pores to the surface of Cokes I, II and VI are summarized in Table XIII.

TABLE XIII. - Surface Area Contributions by Various Ranges of Pore Size.

Coke.	Surface of Pores in Size Range Indicated			
	< 0.1mm.	0.1 - 0.2mm.	0.2 -1.0mm.	Upper Rang
I	81	32	19.4	9.6
II	111	38	26	10.0
VI	33	30	27.0	9.0

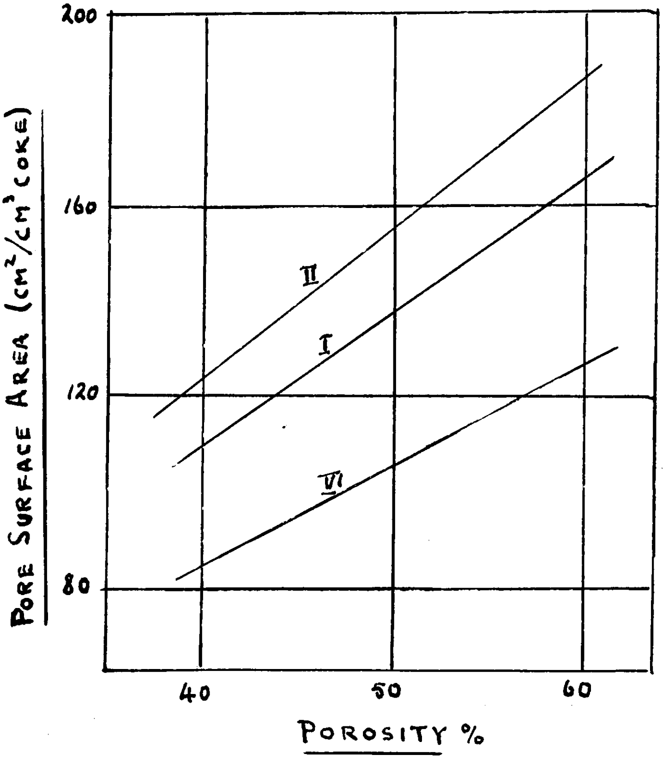
The range < 0.1 mm. corresponds with those maxima mentioned above and they are clearly shown to make the most variable contribution to surface area. The contribution is also of most doubtful effect however, as these are the very pores which, it has been argued may owe their existence to the fact that they were virtually sealed off at the time of their formation. If they are still sealed off or accessible to reacting gases only with difficulty, then there is scarcely any difference among the effective surface areas of these cokes. Even by virtue of their size these pores must be of low availability and their contribution to effective or active surface is probably much smaller than straight calculation suggests.

No suitable test has yet been devised to measure the availability of pore surface to reacting gases. Availability of pore volume would be easier to assess but of much less use. A type of technique which might lead to the desired information would be one involving sorption and de-sorption of gases on the surfaces being examined. It would depend on diffusion rates and results would probably be very difficult to interpret. Comparing as extreme cases Cokes II and VI it can be shown that surface "availability factors" in the ratio 1:2 would make their available surfaces approximately equal. Inspection of the appropriate figures in Tables XII and XIII suggests that such values for the availability factor as, say 0.3 for II and 0.6 for VI would be quite possible and it is therefore not at all certain that the surface of II is effectively greater than that of VI. Until a suitable test of accessibility is devised the usefulness of these distributions cannot be properly assessed.

The effect of porosity alone on pore surface area is demonstrated in Figure 11. The three curves represent the pore surfaces of series of cokes having pore distributions like Cokes I, II and VI, and in each case bubble porosities from 40 - 60°/o.

FIGURE 11.

Effect of Porosity and Pore Size Distribution on Pore Surface Areas.



Pore surface is in each case proportional to porosity but it will be noted that the distribution can be of greater importance than porosity. It is particularly notable that a coke with a distribution like VI and 60% pores, would have as small a pore surface area as one with a distribution like II and only 40% pores. These are extreme cases that possibly could not be realized in practi~~s~~e but they do help to stress the potential /c importance of distribution and justify the assertion of Ramsberg andSperr in 1917 that the determination of porosity alone was valueless.

The significance in the difference in the pore distributions of "good" Durham and Welsh, and "poor" Scottish coke cannot properly be assessed at this stage. That it *is* a contributory factor seems very probable but there is no evidence yet that it is a major factor. Future investigations must assess the availability of surface to reacting gases and then attempt to correlate available pore surface and reactivity. It may well be that some other factor such as chemical composition or the presence of catalysts is of much greater importance than surface area.

The surface due to intermicellar pores has not been considered. This must be of very great extent, but very inaccessible. Its effect on the combustion of coke is quite incalculable however and both the nature of these fine pores and their possible effects on the combustion properties of the coke would be worthy of further investigation.

SECTION 15.

THE AVERAGE CELL WALL THICKNESS.

The cell wall thickness can be calculated only if the pores can be assumed (as in Section 14) to be spherical or to have some other simple shape, and to be uniformly disposed so that the cell walls are of approximately the same thickness throughout. The former assumption is valid for the smaller pores and it can be shown that it is their volume and size distribution that are most important in determining the cell wall thickness. The latter assumption cannot readily be justified but it is believed that the calculations yield values which are at least comparable from coke to coke.

Using the same symbols as in the previous Section and considering unit volume of a representative portion of coke -

The total volume of pores of diameter d $= P\sum_d p$

Consider the coke to be built up entirely of a large number of cenospheres each with a shell $c/2$ thick where c is the cell wall thickness of the coke.

The total volume of these cenospheres $= \sum_d \frac{\pi}{6}(d+c)^3 \times \frac{6pP}{\pi d^3}$

$= P\sum_d \frac{p(d+c)^3}{d^3}$

But this equals unity,

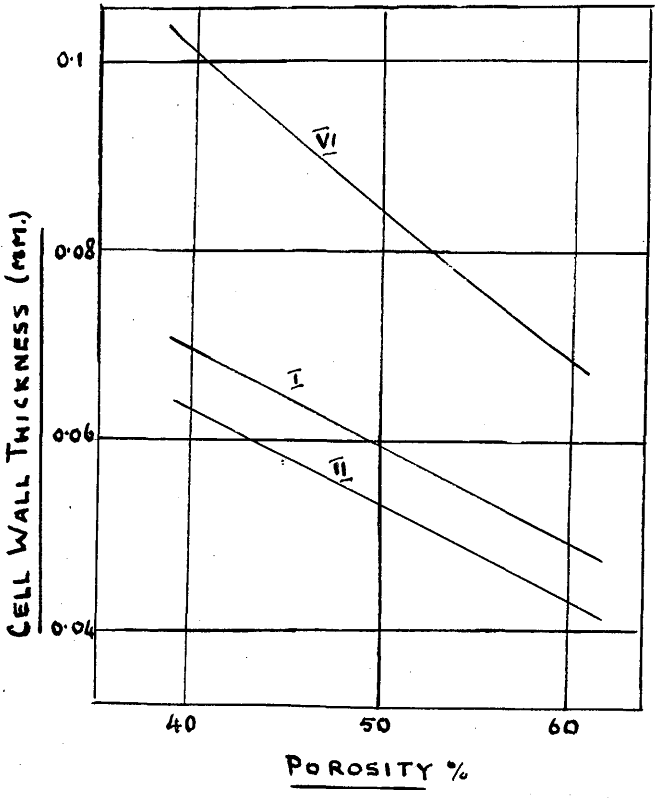
therefore $P\left(\sum_d p + 3\sum_d \frac{p}{d}c + 3\sum_d \frac{p}{d^2}c^2 + \sum \frac{p}{d^3}c^3\right) = 1$

i.e. $\left(3\sum_d \frac{p}{d}\right)c + \left(3\sum_d \frac{p}{d^2}\right)c^2 + \left(\sum_d \frac{p}{d^3}\right)c^3 = \frac{1}{P} - \sum p = \frac{1}{P} - 1.$

Now the evaluation of $\sum_d \frac{p}{d}$ was demonstrated in the previous Section and those of $\sum_d \frac{p}{d^2}$ and $\sum_d \frac{p}{d^3}$ can be carried out in the same way. The value of P is known for each coke. Hence c

FIGURE 12.

Effect of Porosity and Pore Size Distribution on Cell Wall Thickness.



can be obtained by solving the above cubic equation. This is readily done using a graphical method.

The values of c so obtained have been included in Table XII. These may again be in some slight error inversely proportional to that in $R = 0{\cdot}4$.

Ignoring Coke P it is seen that the maximum value of c is about twice the minimum. Again Scottish cokes and the Durham and Welsh cokes form two separate groups.

The separate effects of porosity and size distribution can again be demonstrated. In Figure 12 the cell wall thicknesses corresponding to porosities from 40 - 60°/o and distributions like those of I, II and VI are presented graphically. The pattern is similar to that obtained for pore surface areas and requires little comment. The value of c is very much affected by the number of small pores - and unfortunately by whatever errors are made in their assessment.

It was thought that this property might be of some importance in determining the "strength" of the materials - particularly their abrasion strength. The samples available were not suitable for a Cochrane test and it was thought that the "Northern Coke Committee's Micro-Hardness Test" (28) would be the most appropriate with which to test the hypothesis. That test had to be modified in some respects. It was not possible to apply it to coke large enough to contain the whole range of pore sizes but a size was chosen (1/16" - 3/32") which would include all the lower range of pores and in which the cell walls are practically the same thickness as in large coke. The size used in the standard test is only 14/25 mesh. The weight of sample used was increased from 2 grams to 10 grams because of the bigger particles. The coke was charged into the standard size of steel tube - 12" long by 1" diameter along with 10 steel ball bearings each 3/8" in diameter. The tube was rotated round the mid-point of its axis at a rate of 28 times per minute.

The effect of the number of turns given the tube on the distributions of the degraded coke was examined in some preliminary experiments and it was decided to measure only the -22m. and -72m. fractions. In each test the coke was hand sieved after (about) 100, 250, 450, and 600 turns and returned to the machine for further degradation. Tests were carried out in duplicate for each coke and plots were made of the -22m. and

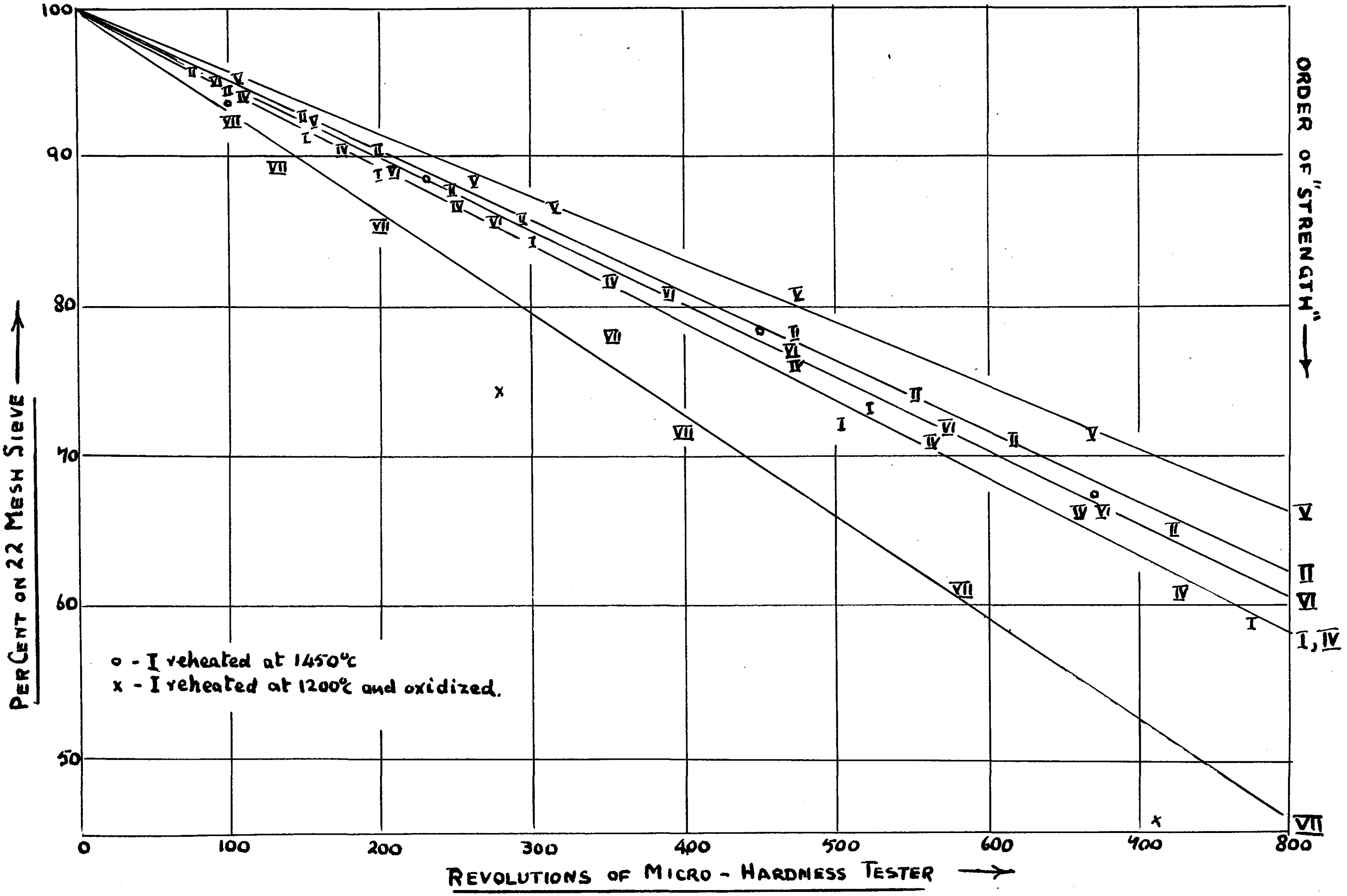


FIGURE 13. - The Micro-Hardness Test.

—72m. fractions against the number of turns given the tube. Figure 13 shows the plot of the —22m. fraction. The 72m. plot was very similar and has not been included.

This simple test has proved sufficient to differentiate the cokes according to their relative "micro-strengths". The significance of that term is rather obscure. The coke in test is subjected mainly to impact forces and partly to forces of self-abrasion. It is important that its degradation from the size charged is not dependent upon pre-formed fissures and cracks as is the case with the larger scale strength tests. The present test is an attempt to compare the cellular structures of the cokes rather than their strengths in the massive state.

Figure 13 shows Coke V to have the highest "micro-strength"; Cokes II and VI are next in order followed by I and IV, with Coke VII the beehive coke by far the weakest of the six.

This ordering of the cokes obviously correlates very poorly with that by cell wall thickness. It may be pointed out however that the strong cokes V, II, and VI are those which have high real density. This suggests that the inherent hardness of the coke-carbon is at least as important as cell structure in determining micro-strength. This inherent hardness is probably a function of coking temperature and may be closely related to real density. Data from six cokes is insufficient on which to test the correlation of micro-strength against both of these variables but two additional experiments were conducted to investi~~age~~gate its dependency upon them.

In the first a sample of Coke I was reheated at 1450°C out of contact with air, and its strength determined. It was found to have increased to a value similar to that of II and VI. Its density had also increased. (Mark X on Figure 13)

Secondly a similar sample which was being reheated at 1200°C was accidentally oxidized. Its strength was measured also and found to have decreased considerably (in spite of increased density). (Mark O on Figure 13). This is attributed to a general reduction in its cell wall thickness due to the oxidation.

These tests suggest that both factors studied affect the micro-strength of coke but it cannot be deduced to what extent each is important. It would be necessary to investigate the inherent strength of the coke-carbon and find a means of equalizing it in all the cokes (e.g. by re-coking at very high temperature) before re-testing the strength / cell wall thickness correlation. It has not yet been possible to carry out this work.

The significance of this measurement of strength and the value of the attempted correlation may both seem rather doubtful, but it is logical to expect that the strength of large pieces of coke should be related to the strength of the cellular material of which they are composed. This applies particularly to their ability to resist grinding or crushing forces and "chipping" forces such as minor impacts incurred during handling. But it probably applies also, albeit in a somewhat lesser degree to resistance to cracking and shattering under major impact forces.

SECTION 16.

GENERAL CONCLUSIONS.

While each of the last few section have been devoted to the drawing of conclusions from the experimental data it may be useful to summarize the more important findings and put them in perspective with one another and with the industrial problems of which they are a part.

The most important result of the research is that for the first time a method has been developed for the measurement of pore size distribution in coke. Assumptions made and accuracy attained at various stages have been discussed in the appropriate sections. The overall effect of these is however rather obscure. The method is a substantial advance on the classification of Malleis but ought to be accepted with some reserve and the results obtained by it used with caution until they can be confirmed by some independent technique. Unfortunately it is very difficult to conceive any other method likely to yield more certain results.

The distributions obtained by this new method are unexpected and very interesting. There are three distinct ranges of pore sizes - the upper and lower ranges of "bubble" pores and the very small "intermicellar" pores. Of the last named scarcely anything is known, except that they account for about 0.5 - 3.5 per cent of porosity in the various cokes examined. The distribution in the lower range of bubble pores only, have been fully worked out, but if large samples were employed and a special set of screens prepared, the method might be used to measure the distribution in the upper range also.

The general form of distribution obtained is remarkably similar in all six metallurgical cokes examined. The proportions of bubble porosity in each range varies only between 40 and 60 per cent of the total. The size limits of each range are similar from coke to coke, and the distributions are all such that there are no pores detected of sizes between about 0.6 and 1.0mm. These features recur in such a definite manner that their significance is beyond doubt.

The most obvious difference among the cokes appears in the distribution of sizes in the lower range. The proportion of pores of size less than 0.1 mm. is very much higher in the three Scottish cokes than in the Durham and Welsh cokes. This difference occurring as it does between two groups is probably very significant. The distribution of these smallest pores was the most difficult to determine, the measurement being subject to the uncertainties in the calibration of the finest sieves and the general difficulty in counting the smallest sizes of particles. The modes at about 0.05 mm. may therefore be rather inaccurate and comparison *within* the two groups can hardly be justified.

Unfortunately the derived values of pore surface area and cell wall thickness depend very much on the proportion of these smallest pores the distribution of which may have been measured rather inaccurately. Nevertheless if the difference in pore distribution between the Scottish and Durham-Welsh groups is accepted as significant then so must the differences between the groups with respect to pore surface area and cell wall thickness. The calculations made have shown that the Scottish cokes have much greater pore areas and thinner cell walls than the Durham and Welsh cokes. The importance of these properties in terms of reactivity and strength cannot yet be assessed but it is interesting to note that Scottish cokes are generally considered to be inferior to Durham and Welsh cokes as blast furnace fuels.

The alleged superiority of beehive coke is not explained by the results reported, for Coke VII is not very different from the other cokes in its group. The lower limit of its bubble pore sizes is rather higher than in the other cokes but this single observation cannot be regarded as significant.

Further investigation of these distributions would be very useful. A much wider range of cokes or other chars should be examined and correlation of distribution of pore sizes with strength and reactivity sought. The possible value of the distributions in helping to elucidate coking mechanism has already been mentioned . In a sense this research lies midway between the two extremes of practical coke-making and blast furnace operation, and may seem to be far removed from useful application in either direction. Disposed in this way however the work has a double importance and it is unfortunate that it has not yielded more positive results.

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Of the various side issues to the main theme of the research the investigation of ~~real~~ apparent density is probably the most important. The geometric method used is not fundamentally new, but the planing of the wax to the level of the coke makes it more exact than has been previously reported. The determination of the inevitable sampling errors is useful in demonstrating the need for methods which can be applied to good average samples of broken material. The suggestion that bulk density measurements could be used for the indirect determination of apparent density may prove to be of practical value.

The measurement of density by the displacement of Diakon is new and might have other applications but these will be limited by the capacity of the material under test to resist deformation under the high moulding pressures required.

The counting technique employed has successfully measured W_s at smaller sizes than previously reported and could be used with refinement at still smaller sizes. This technique could be used to obtain useful information on shape factors of particles, and another application is illustrated in Appendix B.

In Appendix A, the investigation of real density determination has made little positive advance on previously published work. The experiments on sieving mechanism described in Appendix B were designed primarily to show the best sieving technique for use in the main research and were thus far successful. The sieving times deduced to be necessary were very much longer than are generally employed and the results suggest that the question of sieving methods requires very full investigation.

APPENDICES.

APPENDIX A.

AN INVESTIGATION INTO METHODS OF DETERMINING THE REAL DENSITY OF COKE.

The real density of coke is conveniently determined by the method given in B.S.S. 735/1937. Briefly, about 5 grams of coke ground below 72 mesh are weighed into a density bottle and covered with water which is boiled gently for half an hour to expel air from the pores and interstices. The bottle is then cooled, filled with water and weighed. The capacity of the bottle is determined and the density of the coke calculated in the usual way. This standard (boiling) method is much more reproducible than the normal apparent density methods and has been accepted as adequate for porosity determinations . There are many references however to anomalous densities obtained by displacement of liquids other than water, and the question arose as to whether the standard method was the one which gave the truest value of D_r. The field of study was attractive for the further reason that it might lead to useful information on the finest pores present in coke.

Previous workers on this problem have produced a large body of data on the densities of coals and chars. Unfortunately none of them worked systematically through a sufficiently wide range of cokes, coking temperatures or displacement fluids to enable a comprehensive theory to be formulated. In those cases where accuracy of measurement was considered it was admitted to be low - usually so low as to render the significance of the data very doubtful. In the present work the significance is

TABLE XIV- Selection of Real Density Data from the Literature

Liquid	Coke A	CokeB	Cokes C, D		Coke F	Charcoal
	Ref.29	Ref.30	Ref.31, 7		Ref.32	Ref.34
Water	1.852	1.96	1.985	1.841	1.854	1.84
Benzene	1.750	1.96	2.054		1.797	2.01
$C\ Cl_4$	1.837		2.086	1.891	1.647	
$C\ S_2$	1.876			1.941	1.984	2.06
$C_6H_5CH_3$			2.142			
C_2H_5OH				1.892		

still not high because although the accuracy is improved the variations being studied have been found to be smaller than were expected. A selection of the early data is given in Table XIV from which the nature of the confusion will be obvious.

Generally the density obtained by the displacement of gaseous helium is accepted as most likely to be correct because helium has the smallest of all molecules except hydrogen, and has a negligibly small van der Waal's field. It can therefore be expected to penetrate a pore system further than any other fluid except hydrogen, and at the same time cannot be adsorbed on the internal carbon surfaces. Unfortunately the helium method has not been at the disposal of many workers. Smith and Howard (33) found water to give a value the same as or rather lower than helium, and Franklin (35) has obtained only a few values from methyl alcohol significantly higher . Other workers have had to invoke the differences in the properties of the liquids to try to explain the variations in measured density, but there was no way of deciding which liquid gave the truest value.

In the present work helium data are again missing, and the results will have to be considered primarily in relation to the properties of the liquids used. These are listed for reference in Table XV.

TABLE XV - Relevant Properties Of Various Liquids.

Liquid.	Viscosity Poise	Surface Tension Dyne	Dipole Moment e.s.u.	Molecular Volume cc./mol.	Compressibility vol/atmx x10^{-6}
Water	1.0	73	1.85	18.0	40 - 50
Ethanol	1.2	22.7	1.85	58.3	100
Methanol	0.6	22.6	1.78	40.5	80
Acetone	0.32	23.0	2.72	73.6	50 - 80
Ether	low	c. 22	1.10	103.0	160
Benzene	0.65	28.9	0	89.0	87
Octane	0.71	21. 0	0	156.0	180
$C\ Cl_4$	0.97	27.0	0	96.5	90
Xylene	0.81	30.0	0	122.0	75

The most important of these properties are probably molecular volume and dipole moment. The former if large would be expected to prevent the passage of the fluid through the finest of the pores and so give low values of density. High dipole moment on the other hand would favour adsorption on the pore surfaces.

The liquid is then highly compressed locally and tends to give a high value of density. The other relevant properties are -

(1) viscosity, which if high may delay attainment of maximum penetration;

(2) surface tension, which if high would usually favour a high degree of penetration of capillary pores - but

(3) contact angle with carbon, if high would reduce, and if greater than 90° as in the case of mercury would reverse the action of surface tension;

(4) compressibility, which would accentuate the effect of dipole moment if itself high.

The nature and extent of the pore surfaces might also be important in conjunction either with surface tension and contact angle or with sorption.

The contents of Table XV cannot be said to explain those of Table XIV. The position seems to be that the density obtained varies with the liquid displaced; that owing to the possibility of conflicting factors neither the highest nor the lowest value need be the correct one; nor is there any way of deciding which *is* correct without recourse to the special technique of the helium method. By the present work it was hoped to gain a better knowledge of the effects of the above factors and if possible to decide what conditions would be most likely to give comparable results if not true real densities.

In the present investigation the "boiling" method was modified to the "evacuation" method to permit the de-gassing of the sample. About 5 grams of coke ground to -72 mesh in a hammer mill were heated at 500°C for 5 hours in a glass tube which was continuously evacuated by a Hyvac pump. This treatment was sufficient for the purpose, and while possibly more severe than necessary did not have any permanent effect on the coke. The liquid was admitted to the de-gassed coke after cooling and the whole transferred to a density bottle which was filled, held in a thermostat at 25°C for an hour, and weighed. Hygroscopic liquids were protected from the atmosphere, especially in the thermostat, by rubber stoppers, and the bottles were provided with caps to minimize evaporation during weighing. The coke was finally filtered off on a hardened paper, dried and weighed.

The method is rather inelegant especially with respect to the final transfer of the coke but the loss of material at this stage was checked and found to be negligible if reasonable care was taken. A refinement which might be suggested is that the coke be washed into a weighed evaporating dish and the liquid evaporated to dryness.

Mott and Wheeler (7) have discussed sources of error. These have been reduced as far as possible in the present work the employment of a thermostat being of primary importance. Certain liquids however showed poor reproducibility especially methanol and di-ethyl ether. The latter yielded no reliable results at all. In general, tests were carried out in duplicate but if immediate agreement was not attained the reason was was sought, the remedy applied and agreement among three or four more results demanded before a figure was accepted. The accuracy of the data is probably about ± ½%. As this is of the same order as the differences being examined the results must be considered as a whole and too much importance must not be attached to any particular items.

In certain cases it was noted that the penetration of liquids occurred over a prolonged period of up to 12 days. This "drift" has been reported elsewhere (32, 36). Here it was observed in some cokes with water, ethanol and xylene. It was not detected with other liquids and did not occur with these after the coke had been reheated above 1000°C. It could be accelerated and almost completed by boiling the liquid over the coke for about half an hour and this procedure was followed when water and ethanol were being used. The magnitude of the "drift" was not greater than 1% of coke volume. It was thought possibly to be due to the relatively high viscosity of these liquids, but it was not observed with carbon tetra-chloride. Franklin has suggested another explanation in her pore constriction theory which will be discussed later.

Employing the two methods described the following series of experiments were carried out.

(1) The difference between the methods was investigated using Coke I and a wide range of liquids. The data obtained showed that the evacuation method gave a value of density consistently one per cent higher than the boiling method. This difference due to degassing would have been expected greater for liquids which were strongly adsorbed than

for those which were weakly adsorbed. Its constancy suggests that sorption is less important than had been believed. The magnitude of the difference between the methods is not considered of sufficient importance to warrant changing the standard test but it might be worthy of further investigation.

(2) The effect of particle size on the density values obtained by the boiling method was investigated using water and the results are summarized in Figure 14 in which the density has been plotted against log. particle size. The logarithmic scale was chosen only for the convenience of having the points uniformly spaced. No special significance is attached at present to the fact that the points lie close to a straight line.

It has been shown (31) that there is no difference between the densities measured on -60 mesh and on -200 mesh coke, and it was implied that grinding finer than -60 m. was purposeless. It would appear from Figure 14 however that this can be true only if grinding has provided a distribution in which the majority of the coke is so much smaller than 200 mesh that removal or finer grinding of larger sizes would have a negligible effect on the density obtained. The nature of the curve obtained and a comparison of the values of the density of -72 mesh and 240/300 mesh coke suggested that very fine dust would give a very high density value indeed. This was verified with the first runnings from the -72 mesh material through a 300 mesh

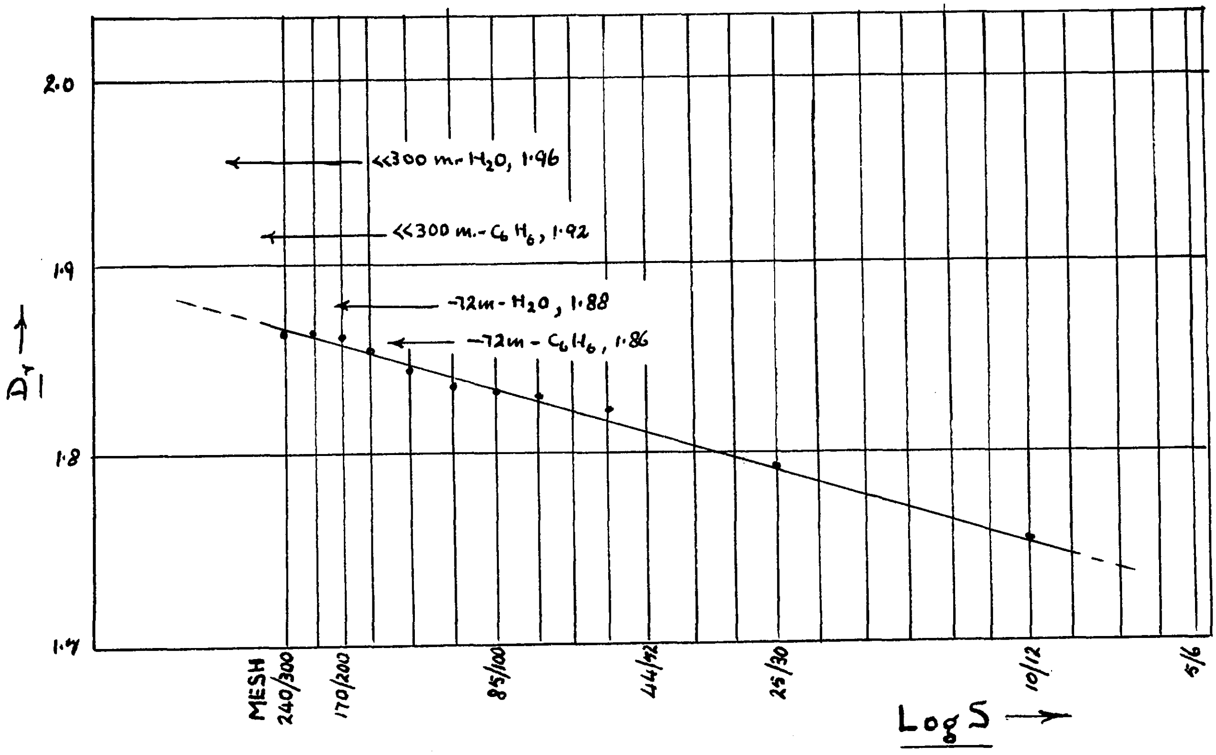

FIGURE 14. - The Effect of Particle Size on Real Density Determinations.

sieve (designated << 300 mesh). The density obtained by boiling this fraction in water was 1.96. The determination was repeated using benzene and the value obtained was 1.92. These figures were higher than those from -72 mesh coke by 0.08 and 0.06 for water and benzene respectively. In either case the increase could be due to greater accessibility of pores, or to increased sorption on the more extensive surface - or to both . If only the former is true the increase is equivalent to the discovery of about 2% porosity (per apparent volume of massive coke) the water being able to enter rather more pores than the benzene. If the higher value of density is due to sorption only, then benzene with zero dipole moment is adsorbed nearly as strongly as water. As both factors may well operate simultaneously however, the small amount of data presented is quite inadequate to solve the problems posed.

It was decided not to alter the practice adopted by others and already in use when the above was completed, of grinding to -72 mesh. Grinding was carried out in a hammer mill and the production of a substantially finer powder without contamination would have been difficult. To employ only a relatively coarse fraction such as 240/300 mesh, would always introduce a sampling uncertainty and the choice of such a fraction could only be arbitrary. The procedure is not satisfactory as the size distributions of different cokes broken down in the same way are certainly different. It was noted that a harder coke (V) gave a much smaller increase in density as measured on $\ll 300$ mesh over that from -72 mesh. This could be due to differences in porosity, surface condition or size distribution. The example is mentioned only to stress the complexity of the problem.

One consequence of this variation in measured density with particle size must be that size segregation becomes an important factor affecting reproducibility of determined densities of any given sample. Samples should always be well mixed before a portion is taken for density determination.

Fortunately it was found that the values of D_r were not required for the determination of bubble porosity for the main investigation and this problem was not studied further.

(3) The effect of re-coking in vacuo at different temperatures on the densities obtained by the evacuation method and using various liquids, was examined. Coke I was employed as received and after granular coke had been re-heated in vacuo at 1000°C, 1100°C and 1200°C and at 1450°C in a sealed tube i.e. in a CO - N_2 atmosphere. The data obtained are summarized in Table XVI.

TABLE XVI. - Densities of Coke I after Re-heating.

Liquid	Temperature of Re-heating.				
	I As rec'd	Ia 1000°C	Ib 1100°C	Ic 1200°C	Id 1450°C
Water	1.90	1.90	1.91	1.96	1.965
Ethanol	1.885	1.91	1.91	1.995	2.00
Methanol	1.90	1.90	1.89	1.995	1.97
Acetone	1.89	1.91	1.90	1.98	1.95
Benzene	1.88	1.91	1.90	1.98	1.975
Petroleum Ether	1.88		1.895	1.98	1.96
Carbon Tetra-Chloride	1.865		1.875	1.93	1.945

Unfortunately no initial coking temperature was known for Coke I but it must have been in the range 900 - 1100°C so that the effect of re-heating to the latter temperature has been small. The coke as received had a density 1.9 by water and rather lower values were obtained by other liquids except methanol. After heating at 1000°C and 1100°C the densities appeared to increase slightly and all liquids except carbon tetra-chloride gave practically the same value. Re-heating at 1200° however caused a big increase in the density as measured by every liquid and a significant change in the order of the densities, that by water becoming lowest (except for C Cl_4) those by the alcohols considerably higher while the figures by benzene, petrol and acetone lay in the middle of the range. The further heating to 1450° was unfortunately not in vacuo. While the same high densities were obtained the order was slightly different again. It is perhaps doubtful if these differences are really greater than experimental error.

It is obvious that these data are insufficient on which to base any complete theory and indeed only a few elementary deductions can be made.

That the measured density increases abruptly somewhere between 1100° and 1200°C is readily apparent but it is not clear what is the nature of the change or why it should be completed within such a short temperature range. It would be expected that if the increase was due to a closer approach being made to a graphitic type of molecular structure it would have continued at higher temperatures. It cannot be due primarily to loss of volatiles under vacuum conditions since the heating at 1450° was not in vacuo, and Franklin (36) coking in nitrogen did find a continuous increase in density with temperature of carbonisation.

It can also be said that the heat treatment modified the factors affecting either the penetration or the sorption of the liquids, for their order with respect to the densities they gave was changed. The most notable feature was that the value given by water after heating at 1200° was one of the lowest in spite of its having a small molecule, a high surface tension and a high dipole moment. The only other factor which might have an effect is the contact angle coke/water, and a short study was made of this property.

Smooth surfaces of coke were prepared by allowing slurries of the different cokes in water to dry out in the depressions of a spotting plate. Drops of water were laid on these surfaces and observed. In most cases they sank into the coke as into blotting paper. With Coke Ic however and with solid electrode graphite, they behaved differently, sitting up on the surface and showing very high contact angles of up to 135°. On other cokes, particularly Ia the drop hesitated for a second and then sank slowly into the powder. Mineral graphite was observed to have a contact angle against water of about 40°.

It will be noted that the measure of contact angle is only as between those above and below 90° with cases like Ia probably close to 90°. Exact values above 90° are not very reliable because of the kind of surface. The effect of particle size was examined and ascertained to have no influence on the phenomenon in the range of sizes affected. The effect of mixing the slurry with say benzene instead of water was to bring other cokes into the same class as Ia.

While these observations fail to explain the densities obtained for Coke Id and give no indication why Ia should differ from Ib in contact angle but not in density, they do point to contact angle as being one of the most important factors affecting these density determinations. Its accurate determination would be very difficult and the factors controlling its value are not known.

Apart from this phenomenon which affects only the densities by water the other factors mentioned earlier must combine to bring about the ordering of the densities obtained. There is a tendency for the polar liquids to give the highest densities and those with the largest molecules to give the lowest. Carbon tetra-chloride is an exception and it can only be suggested that the presence of four chlorine atoms in its molecule renders it effectively larger than is indicated by the value of its molecular volume.

(4) The densities of the cokes used in the main research were determined by the evacuation method with water and benzene in all cases and with a number of other liquids also on Cokes I, II, and VII. Some data were also available from a sample of a Coke III obtained from the same source as II at an earlier date. The results of these tests are summarized in Table XVII.

The densities obtained were in nearly the same order in Cokes I, II, and VII with respect to the seven liquids used, but V and VI gave the water and benzene figures the same, and the densities of Coke III were ordered rather like those of Ic. This suggests a higher effective coking temperature

TABLE XVII.- Real Densities of Cokes I - VII using Various Liquids.

Liquid	I	II	III	IV	V	VI	VII
Water	1.90	1.95	1.93	1.90	1.96	2.01	1.92
Ethanol	1.885	1.95	1.95				1.90
Methanol	1.90	1.97					1.91
Acetone	1.89	1.97	1.96				1.90
Benzene	1.88	1.94	1.95	1.885	1.965	2.01	1.88
Pet. Ether	1.88	1.94					1.865
$C\ Cl_4$	1.865	1.92	1.935				1.865

for these cokes though not necessarily a higher absolute temperature. The ordering of densities in III is most interesting as it has certainly not been affected by the conditions of a laboratory treatment. It is regretted that none of that coke was available for contact angle determination. The position of carbon tetrachloride as giving the lowest densities is maintained but still cannot be explained.

CONCLUSIONS.

Considering the results of these experiments as a whole it is surprising that the range of density values obtained from any one coke has been so narrow, in view of the wide ranges obtained by earlier workers. The reduction of this variation has rendered the improved methods by which it was obtained inadequate to explain the small differences which remain - if indeed even they are real.

In view of this it would seem to be of little consequence which liquid is used for the determination of real density for calculation of porosity - especially when the inaccuracy of the measurement of apparent density is considered. Until more information on the contact angle variations is available however, the densities by water may be suspect. It is not suggested that a change in the standard method is desirable but only that further investigation is necessary, and that densities by non-polar substances of large molecular volume such as benzene may be more comparable for research purposes as they are less likely to be affected by the surface condition of the coke. The alcohols might do equally well but densities higher than that by helium have been reported obtained by methanol. The benzene figures have been accepted (with reservations) as the values of D_r of the cokes employed in the main research.

The "drift" phenomenon, the dependency of the density value obtained upon particle size, and the difference between the results by the boiling and evacuation methods support the contention that a very fine pore structure exists in coke. That its dimensions may approach those of molecules has already been shown by Franklin (36). It was the possible existence of a substantial volume of such fine porosity that pointed to the necessity of developing a method for measuring the apparent density of small particles. (Section 6)

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Further discussion of the differences between liquids and

and between cokes can only be highly speculative. It might be suggested that there was a high and a low temperature form of coke, but the sample re-heated at 1450° does not fit such a classification very neatly.

The most thorough work on the problem to date has undoubtedly been the recent contribution of Franklin (35, 36) firstly on coals and later on cokes. She has developed a very neat theory consistent with her own data and which may be summarized as follows.

Increased coking temperature increases real density but causes progressively narrowing constrictions to form in the finest pores. These deny access to the inner pore space to all liquids with a greater than critical molecular diameter. As the coking temperature is raised and the constrictions become narrower liquids are excluded one after another in order of their increasing molecular volumes and so give low density values compared with those of molecular volume lower than critical. Under conditions where molecular diameter was critical prolonged "drift" was explained as being due to seepage of the liquid through the widest of the constrictions. At the highest coking temperatures the density measured was found to be independent of the fluid used except that helium after prolonged "drift" usually gave a higher value. Cokes prepared at low temperatures sometimes gave higher densities by methanol than by helium and it is possible that other liquids too were adsorbed though not with such marked effect.

In a few details the present data do not conform with that theory. The low densities obtained using water, the densities by carbon tetra-chloride, and the fact that all liquids do not give identical values of density for cokes re-heated to high temperatures, fail to support it. It is believed that her theory is generally correct however but that more extensive work would probably show that the other factors like dipole moment and surface tension were combining to modify it. Franklin's work was carried out on only three cokes all prepared under laboratory conditions. A criticism is that they were prepared in nitrogen from coal already ground to -72 mesh. The "constrictions" may be a surface phenomenon only, and not permeate the entire pore system. Then in the present work in which the coke was ground after heating to its maximum temperature, the "constrictions" would be destroyed. This would explain why the densities of the higher temperature cokes were at variance with Franklin's theory in <u>not</u> being independent of the displacement liquid.

A much more comprehensive study than has yet been made is necessary to solve these problems concerning the measurement of the real density of chars and cokes and to demonstrate the nature of the fine structures of these materials.

APPENDIX B.

THE MECHANICS OF SIEVING.

When the counting method was first examined it was soon apparent that the value obtained for the average weight W_s per particle in a given size fraction was very much dependent upon how the sieving had been carried out. Hand sieving gave very erratic data and never came to finality for W_s increased continually with sieving time. It was decided to investigate the mechanism of sieving particularly to find out the best technique for use in the main research.

The literature recognizes the problem but provides no very satisfactory solution. Sieving is written off as a "statistical" process whose limitations must be accepted philosophically. Perhaps the best treatment is by Dallavalle (27) but even he does not suggest that sieving times generally employed are rather short.

Examination of the B.S.S. 410/1943 on Fine Mesh Test Sieves shows that owing to manufacturing difficulties the cloths and especially the finest of them are made to rather generous specifications.

Even if screen apertures were exactly uniform sieving would still be a "statistical" process and the time taken for a particular particle to pass a given screen would be a matter of chance. If its dimensions were such that it could fall straight through no matter what its orientation, its time of passage would probably be short. If its length (only) was greater than the aperture so that it could "bridge" the spaces then its probable time of passage would be rather longer. It might be needle-shaped or tabular and of such dimensions that it could pass only if it fell in a particular manner, and in that case the probable time of passage would be very long. The actual time taken by any individual particle cannot be predicted, nor would it be of any interest.

In the case of imperfect screens the process is complicated by the fact that "near size" particles include those which can pass only the oversize apertures and these have a probable time of passage that is very long indeed.

Apart from size and shape, factors affecting the passage of a particle through a sieve aperture include -

(1) The nature of the surface - i.e. rough or smooth, wet or dry, etc.

(2) The possibility of agglomeration depending on electrostatic or magnetic condition of the surface, or on adsorbed layers. This has not affected the present work.

(3) The nature of the motion or vibration of the screens; both frequency and amplitude of vibration have been shown to be important and their effects vary with particle size. (see reference 27)

(4) The particle weight as it affects (3)

(5) The number of other particles in competition (i.e. the load on the screen).

Size, shape, density, and surface condition have been treated as invariables except insofar as they may differ fortuitously among the materials used. Nor could the vibration of the

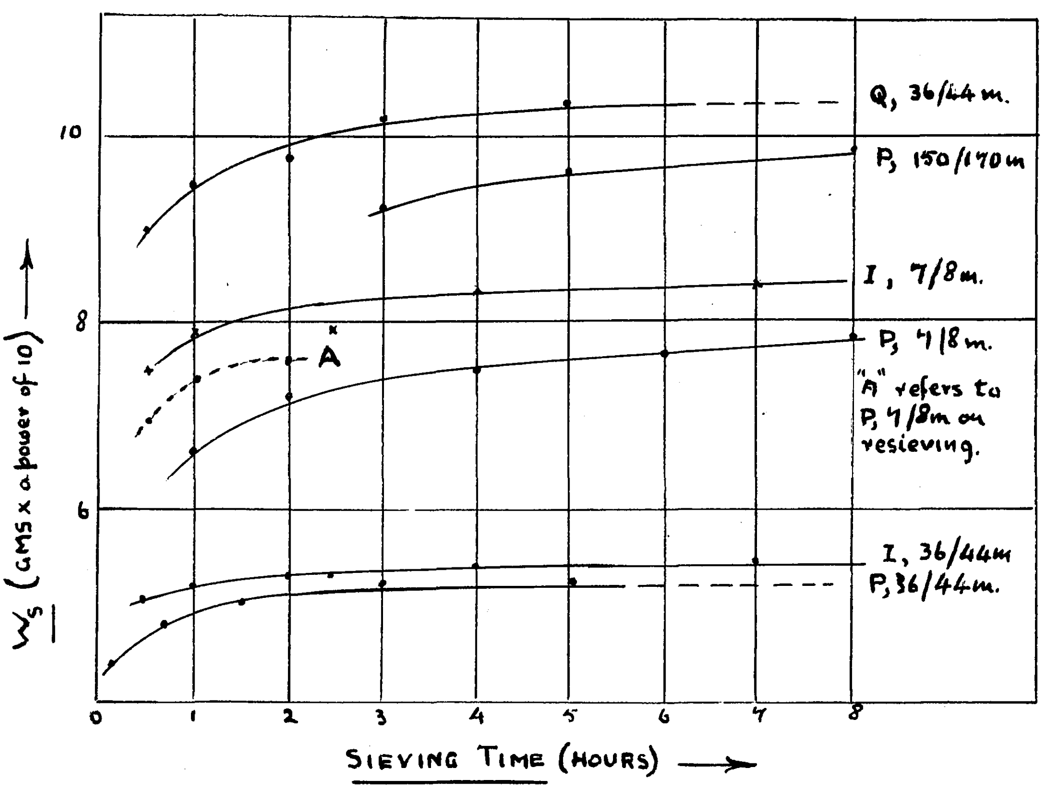

FIGURE 15. - Variation of W_s with Sieving Time.

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screens be varied as the only machine available was a Ro-Tap. The only factors under control were the load on the screens and of course the time of sieving. These have been investigated in three size ranges, the criterion of the degree of completion of sieving being the rate of increase of W_s in a particular fraction with sieving time. As sieving proceeds any size fraction is gaining large particles and losing small ones so that W_s increases until the passage of material is negligible .

Coke I, Coke P (which is non-porous in medium and small sizes) and non-porous Quartz have been used in these tests. The three size ranges employed were -

(1) Large sizes-5/12 m., W_s being determined on the 7/8m.fraction

(2) Medium size -30/52m., W_s determined on 36/44m. fraction
(3) Small size -100/200m. W_s determined on 150/170m. fraction.

The data obtained are summarized in Figure 15, W_s being plotted against sieving time. A selection of the data is also tabulated in Table XVIII to show how the screening analysis varies with time. On Table XIX there are presented the results of a separate investigation into the effect of screen load upon sieving efficiency.

That latter investigation led to the rather unexpected conclusion that load, within the limits studied, did not affect the "rate" of sieving. In practice loads employed were kept well within the limits investigated. It may be pointed out that bulk volume or number of particles would require to be used as a measure of load if materials of different densities were being compared.

Figure 15 indicated that with large sizes the increase in W_s after 2 hours sieving is small but steady. In the case of Coke P abrasion was noticed, the particles becoming rounded. When after 8 hours sieving it was mixed and re-sieved the process was apparently much more rapid than on the first occasion (curve A). Another sample was taken, sieved for one hour and W_s determined. The sample was then mixed, re-sieved and W_s again determined. This was repeated in all eight times. The value of W_s obtained was the same each time. This suggests that friable material may be damaged when actually passing through the screens rather than by self abrasion between them.

TABLE XVIII - Selection of Screening Analyses.

Sieving Time (hours)	% of 60 grams of Coke I, 5/12 mesh fraction					
	+ 5m.	5/6m.	6/7m.	7/8m.	8/10m.	÷ 10m.
0.5	13.4	19.7	22.4	20.6	23.9	1.3
1	10.2	19.7	21.7	21.5	24.8	1.8
2.5	9.4	19.5	20.6	22.7	25.2	2.5
4	8.9	19.0	19.6	23.7	25.6	3.0
7	8.4	19.1	18.8	24.1	25.9	3.6

	% of 27 grams of Coke I, 30/52 mesh fraction			
	+ 36m.	36/44m.	44/52m.	÷ 52m.
0.5	37.8	33.6	26.1	2.1
1	30.7	37.3	27.4	4.6
2.5	28.6	38.1	28.1	5.8
4	22.8	38.5	28.4	10.3
7	19.6	39.8	28.6	13.0

	% of 10 grams of Coke P, 100/200m. fraction			
	+ 150m.	150/170m.	170/200m.	÷ 200m.
0.5	42.2	n.d.	n.d.	3.4
1.5	35.2	n.d.	n.d.	6.7
3	29.9	39.8	20.2	10.1
5	25.9	40.4	20.0	13.7
8	22.9	41.0	20.0	16.0

TABLE XIX. - Effect of Load on the Screens.

Size. (mesh)	Total Load (gms.)	Load per Screen (avg.) (gms.)	W_s after 1 hour sieving (gms)
Large. 5/12m.	25	5	0.00750
	50	10	0.00752
	100	20	0.00751
Medium 30/52m.	6.5	2.2	0.0000535
	10	3.3	0.0000525
	22.5	7.5	0.0000527
	26.5	8.8	0.0000515
	50	16.6	0.0000520
	100	33.3	0.0000527

Medium sizes show less change in W_s after 2 hours but there is still a slight increase.

Small sizes were difficult to test because the expected differences in W_s were of the order of the experimental error in the counting. Only Coke P was examined and it would seem that although 3 hours sieving gave a value of W_s significantly smaller than that after 5 hours the increase between 5 and 8 hours can probably be ignored.

The size analyses show that the passage of material even after 7 or 8 hours is appreciable. It has not been possible to determine to what extent this has been due to "statistical" sieving and to what extent to degradation. The total "dust" formed always appeared negligible, but the removal of a very small chip may very often be sufficient to permit the passage of a near-size particle and the accumulation of many such chips might still appear negligible though the effect of their removal had been considerable.

It is surprising that the increase in W_s becomes negligible while the passage of the material through the screens is still appreciably high. This suggests continuous uniform abrasion of all material and consequent size degradation. This is probably the main factor operating after 2 or 3 hours although the amount of dust did appear small. This aspect of the problem must remain unsolved, for with the main purpose of the experiments fulfilled these investigations were brought to a close before the interesting side issues were worked out.

The purpose of the experiments was the determination of the best sieving conditions for use in the main research. Obviously the conditions chosen must be a compromise between the desirable and the practicable, and possibly between under-sieving and over-abrasion. The times chosen have been 3 hours down to 85 mesh and 5 hours between 100 and 200 mesh. The data obtained on Quartz show that it passes the screens rather more slowly than does coke and this may be due to shape or to density. The difference was thought to be of little practical significance after 3 hours sieving however, and the same times were employed for quartz as for coke.

It is of interest that the abrasion of quartz is very unlikely so that prolonged passage of material is not due entirely to that cause. The differences in sieving rates of porous and non-porous materials of the same size, is negligible and gives no information of the possible effects of surface roughness on the size (S) of the average particle produced in any fraction.

These findings need not apply to other materials except in a general way, or to other shaking machines many of which are believed to be much faster in operation than the Ro-Tap.

It is recognized that this investigation of sieving is far from complete. Its purpose was to give guidance in the main research and it has thus far been successful. It does indicate however that sieving times normally employed even on research work are quite inadequate for many purposes and demonstrates that a fair approach to completion is attainable in times which are for research at any rate, reasonable.

Acknowledgements.

The author wishes to express his thanks to Professor R. Hay for his interest, encouragement, and patience at all stages of the work; and to Dr. J. Taylor, who directed the research, for his constant attention, his helpful suggestions and his useful ideas.

Thanks are also due to the British Coke Research Association on whose grant the work was commenced.

The research was carried out in the Metallurgy Department of The Royal Technical College, Glasgow.

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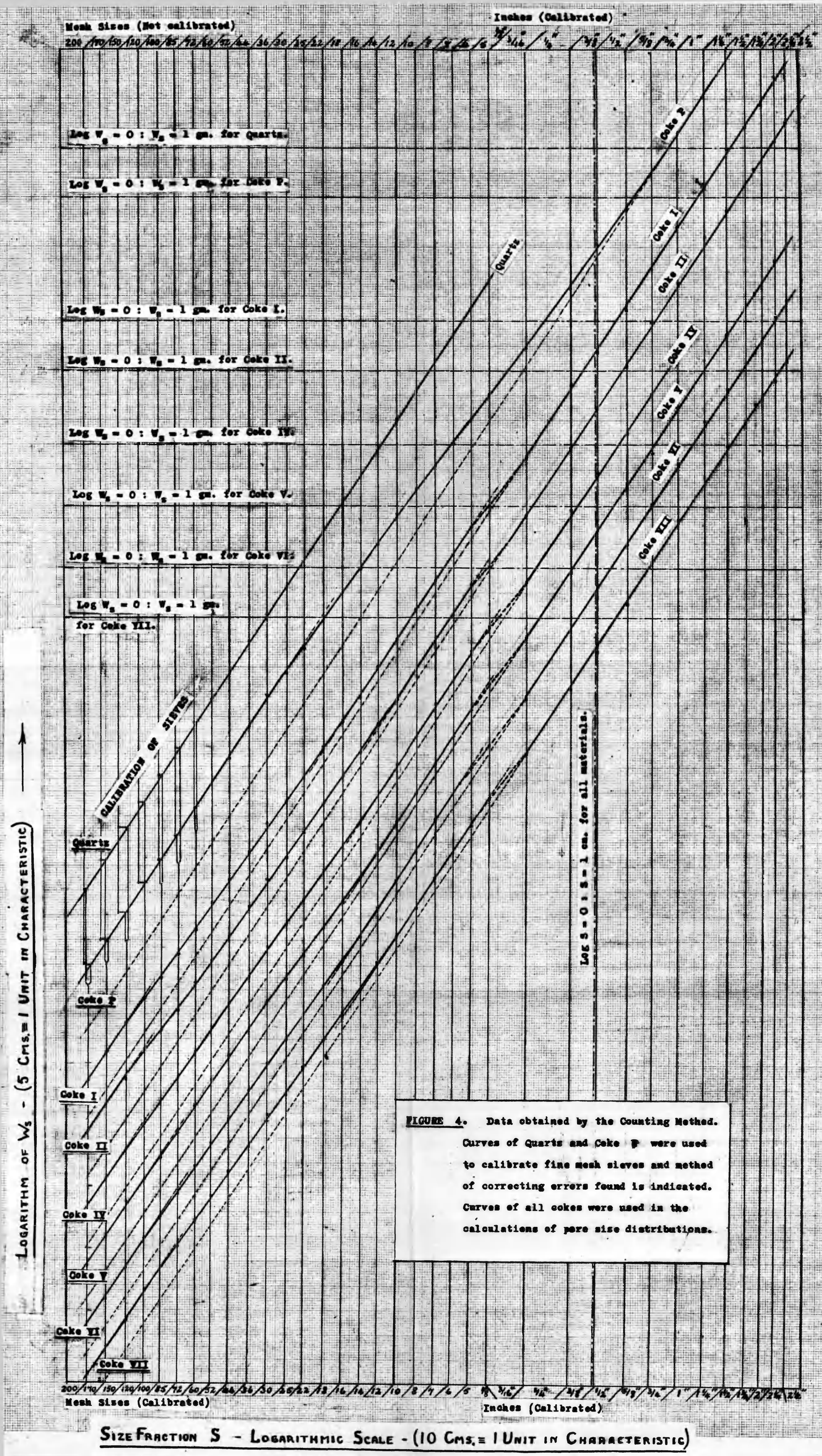

FIGURE 4. Data obtained by the Counting Method. Curves of Quartz and Coke P were used to calibrate fine mesh sieves and method of correcting errors found is indicated. Curves of all cokes were used in the calculations of pore size distributions.