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### EFFECT OF DIFFERENT COKES ON PHYSICAL PROPERTIES OF GRAPHITIZED CARBON PLATES\*

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The effect of twelve different calcined cokes (the coal tar pitch binder being kept the same) has been investigated with respect to the physical properties of graphitized carbon, molded plates produced therefrom. The cokes include materials that are used commercially, at present, as the filler in the manufacture of carbon bodies. Changes in the bulk density, weight and volume of the carbon plates as they proceed from the green through the baked to the graphitized state are presented. True, helium, and apparent density data are presented for the calcined cokes and their graphitized plate counterparts. The gas reactivity, coefficient of thermal expansion, electrical resistivity, and tensile breaking strength of the graphitized carbon plates are related to the specific surface area, total pore volume, total open-pore volume, total closed-pore volume, open macropore volume, and intensity of the (002) X-ray diffraction peak for both the calcined cokes and graphitized plate material. Explanations for the variations in these four important properties of the graphitized carbon plates are presented.

#### I. INTRODUCTION

One of the primary difficulties in duplicating the properties of carbon and graphite products is the great variation in properties of calcined petroleum cokes which are used. Since the coke usually constitutes ca. 85% of the final body, its properties are of extreme importance. Unfortunately, petroleum coke is a by-product of the petroleum industry. It is the residue from a process designed for optimum production of more valuable liquid hydrocarbon products. Its properties are not determined or controlled to give an ideal raw material for the manufacture of carbon and graphite products. Nevertheless, petroleum coke is still the best general raw material that has been found for the graphite industry. Since it is a by-product of the refining operation, this results in its having a lower price than would otherwise be the case,

which is of a distinct advantage to the carbon industry. The fact remains that it is imperative for the carbon industry to be able to relate the properties of calcined petroleum coke to those of the finished carbon and graphite bodies. With this ability, the industry will be able to purchase more wisely petroleum coke supplies, when it has particular applications for the final carbon products in mind.

In this research, twelve different cokes, supplied by various companies, were used. Nine of the samples were produced by the usual delayed coking procedure and represent some of the most important sources of raw cokes now available to the carbon industry. Two additional petroleum cokes investigated were fluid coke and gilsonite coke. One sample of coke produced from coal tar pitch was also used. Throughout the work the same barrel of Barrett No. 30 medium pitch was used as the binder material. Graphitized carbon plate samples were produced from the above raw materials using an identical operating procedure in each case.

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Properties (specific surface area, total pore volume, closed-pore volume, X-ray density, degree of orientation, chemical analysis, among others) of the calcined cokes were compared with properties (specific surface area, total pore volume, closed-pore volume, X-ray density, degree of orientation, reactivity to carbon dioxide, coefficient of thermal expansion, transverse breaking strength, electrical resistivity, among others) of the baked and graphitized carbon plates.

## II. EXPERIMENTAL

### A. Calcining of Raw Cokes

The raw coke samples were calcined using one of four experimental procedures. In procedure A the coke was calcined in an indirect fired retort. The calcination cycle required approximately 12 hr and the coke temperature was controlled to 1100–1300°C. Method B was a direct fired calcination process involving a process cycle of about 5 hr with the coke reaching a temperature of about 1300°C. The furnace used in calcining by the method C consisted of a gas fired crucible melting furnace lined with a silicon carbide refractory. The coke to be calcined was placed in a Tercod crucible, furnace sealed against infiltration of air and a neutral atmosphere maintained by control of the fuel mixture. Cycle was about 6 hr with the coke temperature reaching 1200°C for a period of 2 hr. In Method D the coke was placed in a large metal sagger which was then packed in sand in a large box type kiln. Firing cycle involved several days with the coke reaching a temperature of 1200°C.

### B. Preparation of Plate Samples

The mix formulation consisted of equal amounts (250 g) of 35 × 65 mesh (Tyler Series) and 65 × —200 mesh (60% through 200 mesh) calcined petroleum coke and 170 g of —10 mesh pitch. This is equivalent to 34 lb of pitch per 100 lb of coke aggregate. The petroleum coke particles were placed in a Veeley mixer and preheated to about 125°C for 15 min prior to pitch addition. The

mixing time in all tests was 20 min. After allowing the mix to cool to room temperature, it was broken up until it passed a 20 mesh screen.

The steel mold and plunger were preheated to 120°C prior to introducing the sample. Upon its introduction into the mold the mix was allowed to heat up for 6 min. The pressure was then raised to 1090 lb/in<sup>2</sup> and held for 10 sec and finally raised to 3270 lb/in<sup>2</sup> for 1 min.

The green specimens were placed in clay saggars, sand packed, and loaded into a furnace where a temperature of ca. 900°C was reached within three days. The baked samples were graphitized in a resistance furnace to ca. 2500°C within 48 hr.

### C. Low Temperature Gas Adsorption Apparatus

A standard gas adsorption apparatus was employed and has been described recently<sup>1</sup>. Surface areas were determined from nitrogen adsorption at liquid nitrogen temperatures using the *BET* equation<sup>2</sup>.

### D. Mercury Porosimeter

A description of the design and operation of the mercury porosimeter used has been given recently<sup>3</sup>. The porosimeter was used to determine the volume distribution of macropores in the sample over the radius range 475–150,000 Å and the apparent density of the samples, by mercury displacement under an absolute pressure of ca. 300 mm mercury.

### E. X-ray Diffraction Apparatus

A 164° (2θ) General Electric X-ray diffraction unit, XRD-3, with copper radiation was used to determine interlayer spacings for the carbon samples, as previously discussed<sup>4</sup>.

<sup>1</sup> P. L. Walker, Jr., R. J. Foresti, Jr. and C. C. Wright, *Industr. Engng Chem.* **45**, 1703 (1953).

<sup>2</sup> P. H. Emmett, *A.S.T.M. Tech. Publ.* **51**, 95 (1941).

<sup>3</sup> P. L. Walker, Jr., F. Rusinko, Jr. and E. Raats, *J. Phys. Chem.* **59**, 245 (1955).

<sup>4</sup> P. L. Walker, Jr., H. A. McKinstry and J. V. Pastinger, *Industr. Engng Chem.* **46**, 1651 (1954).

The interlayer spacing and carbon-carbon spacing in the layer plane were used to calculate the true density of the carbon in the standard manner. The intensity of the (002) diffraction peak was used, as previously discussed<sup>4</sup>, as a measure of the tendency of the carbon particles to orient on the glass X-ray slide. Carbon placed on the X-ray slide from both the cokes and graphitized plates consisted of -200 mesh material. As shown presently, this orientation tendency is apparently paralleled by the disposition of the carbon particles to line up with their basal planes perpendicular to the molding direction during sample fabrication.

#### F. Reaction Rate Apparatus

The reactor was the same as that used in previous gasification studies<sup>1</sup>. Plate samples  $1\frac{1}{2}$  in. long by  $\frac{1}{2}$  in. wide by  $\frac{1}{4}$  in. thick were reacted with carbon dioxide at 1000°C and atmospheric pressure. The samples were suspended in the reactor from a  $\frac{1}{4}$  in. diameter two-hole ceramic thermocouple tube. A tungsten wire, which passed through one hole in the thermocouple tube through a  $\frac{1}{16}$  in. hole drilled  $\frac{1}{4}$  in. from the top of the sample, and out the other hole in the thermocouple tube, actually supported the sample in the furnace. Insignificant reactivity of the tungsten wire with carbon dioxide was observed. No catalytic effect of the tungsten wire, where it came into contact with the carbon, was found.

#### G. Helium Density Apparatus

The helium densities were determined by the conventional method in which a measured quantity of helium is expanded into a sample tube of known volume containing a known sample weight. The apparatus (thermostated at  $30 \pm 0.1^\circ\text{C}$ ) was of the constant pressure type; that is, after the expansion of the helium into the sample bulb, the pressure was increased to its initial value by decreasing the apparatus volume using mercury displacement. From the volume of mercury required to return the helium pressure to its

original value, the volume of solid sample plus closed pores (and, hence, its helium density) could be determined. Equilibration time of one hour was allowed after exposing the sample to the helium gas. Helium density determinations could be duplicated to within  $\pm 0.5\%$ .

#### H. Thermal Expansion Apparatus

The values for coefficient of thermal expansion (*CTE*) were determined by measuring the linear expansion in the graphite sample bar upon raising the temperature from 20°C to 100°C. The measurement was made along the 5 in. length of a  $\frac{5}{8}$  in.  $\times$   $\frac{3}{8}$  in.  $\times$  5 in. molded bar. Thus, the measurement was made perpendicular to the molding direction or in the direction of preferred orientation imposed by the molding process. In the *CTE* apparatus used, the specimen is bolted in a jig having an Invar (iron-nickel alloy) base. The difference in expansion between the Invar standard and the graphite specimen is measured by means of an optical lever device. The *CTE* values are reported in units of  $^\circ\text{C}^{-1}$ , with a precision of  $\pm 0.1 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ .

The reported results have been corrected to give values comparable with a *CTE* method previously used in this laboratory in which the measurement was made over the temperature range 100-600°C. Therefore, the results reported herein are comparable within the series since they were all run by the same *CTE* method. They may not necessarily check values published in the literature for other graphite bodies because of differences in material used, manner of sample preparation, and the method of *CTE* measurement.

#### I. Electrical Resistivity Apparatus

The electrical resistivity was determined by a potentiometric method. The sample was placed in a spring-loaded "jig" to insure good electrical contact. A pair of knife-edges of 3 in. span was placed in contact with the sample, and the difference of potential

between the knife-edges measured by a potentiometer. The current through the sample was determined from the voltage drop across a standard resistance in series with the sample.

#### J. Transverse Breaking Strength Apparatus

A plate sample was placed on two knife edges 3 in. apart. Pressure was applied by a third knife edge at the center of the sample and measured by a Dillon fibre stress tester. The knife edges were rounded to a  $\frac{1}{16}$  in. radius.

### III. RESULTS AND DISCUSSION

#### A. Ash and Sulfur Contents in Calcined Cokes and Ash in Graphitized Plates

Table I presents data on the ash and sulfur

TABLE I  
Ash and Sulfur Contents in Calcined Cokes  
and Ash in Graphitized Plates

Sample number	Sample description	Weight % ash		Weight % sulphur
		Cokes	Plates	
(1)	f.c.*	0.20	0.04	3.9
(2)	c.t.p.c.†	0.23	0.10	0.04
(3)	p.c.‡	0.15	0.10	1.2
(4)	p.c.	0.16	0.11	1.2
(5)	p.c.	0.19	0.11	0.85
(6)	p.c.	0.30	0.09	1.6
(7)	p.c.	0.16	0.27	0.17
(8)	p.c.	0.21	0.13	0.24
(9)	p.c.	0.26	0.25	1.5
(10)	g.c.§	1.1	0.20	0.20
(11)	p.c.	0.17	0.06	1.4
(12)	p.c.	0.31	0.10	1.4

\* Fluid coke.

† Coal tar pitch coke.

‡ Petroleum coke.

§ Gilsonite coke.

contents of the calcined cokes and ash in the graphitized carbon plates. The only coke sample which has an unusually high ash content is the gilsonite coke. Fluid coke is seen to have a high sulfur content, and the coal tar pitch coke a very low sulfur content. On graphitization, the ash content in the carbon plates has been materially reduced, as expected.

#### B. Change in Some Physical Properties of Carbon Plates in Going From Green to Graphitized Samples

Table II presents data on the change in various physical properties of carbon plates in going from green to graphitized samples. It is seen that, in all cases, the bulk densities of the plates are decreased upon baking. For most of the samples, the bulk density continues to decrease upon graphitization; but for several of the samples the decrease in volume offsets the decrease in weight and some increase in density is found.

As would be expected, the majority of the weight loss upon heating the green samples occurs during baking, where the preponderance of the volatile constituents of the pitch is released. If it is assumed that all the weight loss during baking is attributed to the release of volatile constituents from the pitch, it is calculated that between 32 and 45% of the pitch is lost during this operation. Anticipating results to be discussed shortly, it is seen that samples (7) and (8), which have the lowest weight loss upon baking, also have the lowest open micropore volume (Table IV) and the lowest closed-pore volume (Table IV) for their graphitized plates. This would suggest that the magnitude of these pore volumes are, at least in part, determined by the weight loss in the binder upon baking.

If it is assumed that the only weight loss in the calcined cokes upon graphitizing the baked plates is a result of removal of the ash and sulfur, the total amount of the pitch volatilized from the samples can be calculated. Table II lists the weight per cent of binder in the final, graphitized plates calculated on this basis. Undoubtedly some additional, small amount of material would be volatilized from the calcined cokes upon graphitization, which would make the figures for per cent binder in the plates too low; but the results are thought to be essentially correct. Again anticipating some results to be discussed shortly, Fig. 1 presents a qualitative relation between total open-pore volume

TABLE II

*Change in Some Physical Properties of Carbon Plates in Going from Green to Graphitized Samples*

Sample number	Bulk densities (g/cm <sup>3</sup> )*			Weight loss (%)			Vol. change (%)			Weight % binder in graphitized plates
	Green	Baked	Graphitized	Baking	Graphitizing	Net	Baking	Graphitizing	Net	
(1)	1.64	1.49	1.48	8.6	5.1	13.7	+0.49	-4.4	-3.9	17.0
(2)	1.70	1.48	1.52	9.8	2.7	12.5	+3.5	-5.0	-1.5	14.8
(3)	1.70	1.55	1.52	8.3	2.7	11.0	+0.67	-1.2	-0.5	17.1
(4)	1.69	1.53	1.51	8.4	3.5	11.9	+0.56	-1.6	-1.0	16.3
(5)	1.65	1.53	1.52	7.8	3.4	11.2	-1.2	-2.5	-3.7	16.7
(6)	1.64	1.54	1.50	7.6	3.8	11.4	-1.7	-0.93	-2.6	17.3
(7)	1.67	1.59	1.59	6.9	1.3	8.2	-1.6	-1.8	-3.4	18.8
(8)	1.70	1.60	1.62	7.2	1.0	8.2	-1.6	-2.0	-3.6	18.9
(9)	1.71	1.55	1.52	9.5	3.5	13.0	+0.31	-1.6	-1.3	15.5
(10)	1.64	1.50	1.59	8.6	5.0	13.6	-0.10	-9.6	-9.7	14.6
(11)	1.75	1.54	1.48	9.4	2.9	12.3	+2.7	+1.5	+4.2	16.2
(12)	1.66	1.55	1.53	7.9	3.1	11.0	-1.8	-1.1	-2.9	17.5

\* Calculated from weight and dimensions of plate.

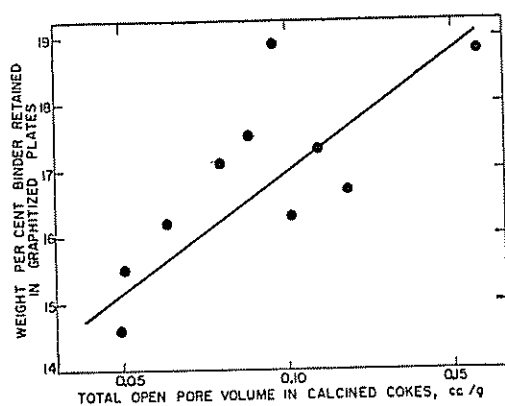


FIG. 1. Qualitative relation between total open-pore volume in calcined cokes and amount of binder retained in graphitized plates.

in calcined cokes (Table IV) and the weight per cent binder in the graphitized plates. The greater the open-pore volume, the greater the amount of binder retained. This suggests that the larger the percentage of pitch which is able to diffuse into the open pore system of the coke, the greater the coking value of the pitch. This is as expected since the deeper the pitch migrates into the pore system of the body, the longer the time required for the volatile products from the

pitch to reach the exterior of the sample. The longer the time the volatile products require to diffuse from the body, the more completely they will be cracked and converted to carbon. Of course, a quantitative correlation of the data shown in Fig. 1 would hardly be expected since the time which the volatile products spend in the body would also be a function of the size and depth of pores from which they originated.

Also listed in Table II are the volume changes of the plates upon baking and graphitizing. With the exception of sample (11), the plates are found to contract upon graphitization. There is a rough correlation between the extent of contraction and the percentage of open microporosity in the calcined cokes. Samples (3), (9) and (11), which show the lowest percentage of open microporosity, also show the least contraction, if sample (4) is disregarded. Samples (5) and (10), which show the highest percentage of open microporosity, show the greatest contraction. Undoubtedly some of the contraction in the plates can be attributed to a decrease in microporosity in the coke particles upon graphitization, as a result of crystallite growth and orientation.

C. *Density Data for Calcined Cokes and Graphitized Plates*

Density data for calcined cokes and graphitized plates produced therefrom are presented in Table III. As is seen, there is little variation in the true densities for either the cokes or graphitized plates. It is thought that the densities for the calcined cokes are in slight error since the ash and sulfur content (and probably a little hydrogen which should be present) are neglected. The density is calculated solely on the basis of the unit cell parameters for the carbon determined from X-ray diffraction data, as previously discussed. It is impossible to decide whether the densities are too high or too low, however.

The true densities for the graphitized plates are quite accurate, because of the small level of impurities in the samples. Furthermore, the densities approach closely the value for natural graphite, 2.269 g/cm<sup>3</sup>, indicating that the samples have been highly graphitized.

In all cases, except sample (11), the helium densities of the calcined cokes are less than those of the corresponding graphitized plates,

as would be expected. Furthermore, there is a rough trend indicating that the higher the helium density in the calcined coke, the higher the helium density in the graphitized plate. The anomalous behavior of sample (11) in showing a decrease in helium density upon graphitization parallels its equally anomalous behavior in showing a volume expansion in going from the green to the graphitized plate. It would seem that this unusual result is attributable to peculiarities in the coke and not in the pitch.

In all cases, except sample (7), the apparent densities of the calcined cokes are greater than those of the corresponding plate samples. This is a result of the introduction of a large macropore volume located in the voids between the coke particles composing the plate samples. Furthermore, as shown in Fig. 2, there is a qualitative relationship between the apparent density of the calcined coke and the decrease in apparent density in going from the coke to the final graphitized carbon body. Of the three samples which fall markedly below the curve but show the same trend themselves, samples (7) and (8) are from the

TABLE III

*Density Data for Calcined Cokes and Graphitized Plates*

Sample	True density (g/cm <sup>3</sup> )		Helium density (g/cm <sup>3</sup> )		Apparent density (g/cm <sup>3</sup> )	
	Cokes	Plates	Cokes	Plates	Cokes	Plates
(1)	2.210	2.267	1.955	2.012	—*	1.487
(2)	2.189	2.267	2.018	2.052	—*	1.575
(3)	2.186	2.268	2.000	2.073	1.724	1.510
(4)	2.183	2.268	2.010	2.067	1.670	1.488
(5)	2.196	2.265	2.014	2.088	1.626	1.514
(6)	2.196	2.268	2.005	2.088	1.644	1.494
(7)	2.199	2.267	2.091	2.167	1.573	1.586
(8)	2.186	2.267	2.046	2.169	1.710	1.618
(9)	2.187	2.268	1.983	2.091	1.801	1.535
(10)	2.205	2.262	1.923	2.078	1.756	1.604
(11)	2.191	2.268	2.070	2.035	1.829	1.500
(12)	2.198	2.268	1.983	2.090	1.687	1.543

\* Unfortunately apparent densities could not be determined on these cokes since the only particle size material available was the coke flour. This was too fine to be used in the mercury porosimeter since the mercury would float the material up the dilatometer tube.

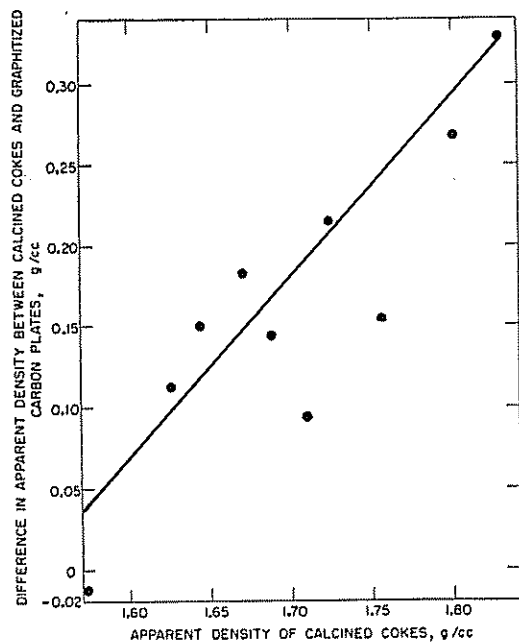


FIG. 2. The effect of apparent density of calcined coke on the decrease in apparent density of the graphitized carbon plates over that of the calcined coke.

same petroleum source and sample (10) is gilsonite coke. The correlation shown in Fig. 2 is as expected. Looking at a coke of the highest apparent density, graphitization would be expected to produce the least additional increase in its apparent density to offset the porosity introduced between coke particles upon packing. On the other hand, for a coke of the lowest apparent density, the combination of a greater increase in its apparent density upon graphitization and the addition of a graphitized pitch binder, probably having a higher apparent density than the calcined coke, offsets the porosity produced between particle voids and results in a density increase. The net result is that the variation in apparent density of graphitized carbon bodies, where the same percentage of binder is added to the green mix, is considerably less than the variation in apparent density of the calcined cokes used to produce the bodies.

#### D. Surface Area, Pore Volume, and Orientation Data on Calcined Cokes and Graphitized Plates

Table IV presents data on surface area, pore volume, and orientation for the calcined cokes and graphitized plates. It is seen that in all cases the specific surface areas of the calcined cokes are greater than those of their graphitized plate counterparts. However, the magnitude of the area decrease in going from calcined coke to graphitized plate is a function of the coke type—the ratio of areas varying from 1.1 for the fluid coke to 6.5 for the coal tar pitch coke. The area decrease could be due to at least four reasons—(1) decrease in surface area of the calcined cokes upon graphitization, (2) blockage of the pore system in the cokes by pitch, (3) decrease in surface roughness of the coke particles by coating with a smooth layer of binder, and (4) lower specific surface area in the graphitized binder than in the calcined coke particles.

Unfortunately, area data are not available for the graphitized cokes, and therefore, the extent to which point (1) resulted in an area decrease cannot be judged. It is known, however, that specific surface areas of carbons do decrease upon graphitization as a result of crystallite growth and orientation. Qualitatively, the higher the calcined coke surface area the greater its decrease in area upon graphitization should be. From Table IV it is seen that cokes (5) and (10) have the greatest surface area and also the greatest decrease in area in their graphitized plate counterparts, which suggests that point (1) is an important factor in determining area change.

If points (2) and (3) are important in effecting an area decrease, it would be expected that a semi-qualitative correlation would be found between the area decrease and total open micropore volume in the calcined cokes (most of the surface area concentrating in the micropore volume as opposed to the macropore volume). Data in

TABLE IV  
Surface Area, Pore Volume, and Orientation Data on Calcined Cokes and Graphitized Plates

Sample	Specific surface area (m <sup>2</sup> /g)		Total pore volume (cm <sup>3</sup> /g)		Total open-pore volume (cm <sup>3</sup> /g)		Total closed-pore volume (cm <sup>3</sup> /g)		Total open-micropore* volume (cm <sup>3</sup> /g)	
	Cokes	Plates	Cokes	Plates	Cokes	Plates	Cokes	Plates	Cokes	Plates
(1)	1.5	1.4	—	0.2314	—	0.1755	—	0.0559	—	0.1515
(2)	1.7	0.26	—	0.1938	—	0.1476	—	0.0462	—	0.1457
(3)	1.6	0.80	0.1225	0.2214	0.0800	0.1799	0.0425	0.0415	0.0789	0.1463
(4)	1.7	1.1	0.1407	0.2311	0.1013	0.1882	0.0394	0.0429	0.0904	0.1583
(5)	2.3	0.69	0.1596	0.2190	0.1185	0.1816	0.0411	0.0374	0.0417	0.1643
(6)	1.9	1.4	0.1529	0.2300	0.1095	0.1920	0.0434	0.0380	0.0964	0.1648
(7)	1.9	0.50	0.1809	0.1894	0.1575	0.1690	0.0234	0.0204	0.1397	0.1690
(8)	1.4	0.36	0.1273	0.1769	0.0960	0.1570	0.0313	0.0199	0.0905	0.1570
(9)	2.0	1.5	0.0980	0.2106	0.0509	0.1733	0.0471	0.0373	0.0509	0.1395
(10)	3.2	1.2	0.1160	0.1814	0.0495	0.1423	0.0665	0.0391	0.0318	0.1274
(11)	1.4	0.80	0.0903	0.2260	0.0636	0.1753	0.0267	0.0507	0.0636	0.1635
(12)	1.3	0.84	0.1378	0.2074	0.0885	0.1696	0.0493	0.0378	0.0663	0.1448

\* Volume behind pores greater than 475 Å in radius.

TABLE IV contd.

Sample	Total open-micropore volume (cm <sup>3</sup> /g)		Open microporosity(%)		Closed-pore volume in total pore volume (%)		Closed-pore volume in total sample volume (%)		(002) X-ray peak intensity	
	Cokes	Plates	Cokes	Plates	Cokes	Plates	Cokes	Plates	Cokes†	Plates‡
(1)	—	0.0240	—	13.6	—	24.2	—	8.3	29.1	168 <sup>1</sup>
(2)	—	0.0019	—	1.3	—	23.8	—	7.3	21.6	216
(3)	0.0011	0.0336	1.4	18.7	34.7	18.7	7.3	6.3	35.0	3178
(4)	0.0109	0.0299	10.8	15.9	28.0	18.6	6.6	6.4	46.0	3585
(5)	0.0768	0.0173	64.8	9.5	25.8	17.1	6.6	5.7	39.6	3342
(6)	0.0131	0.0272	12.0	14.2	28.4	16.6	7.1	5.3	46.7	2983
(7)	0.0178	0.0000	11.3	0.0	12.9	10.7	3.7	3.2	72.9	4780
(8)	0.0055	0.0000	5.7	0.0	24.6	11.3	5.4	3.3	56.7	4977
(9)	0.0000	0.0338	0.0	19.5	48.1	17.7	8.5	5.7	41.2	2970
(10)	0.0177	0.0149	35.8	10.5	57.3	21.5	11.7	6.3	24.5	1383
(11)	0.0000	0.0118	0.0	6.7	29.6	22.4	4.9	7.6	61.0	4486
(12)	0.0222	0.0248	25.1	14.6	35.8	18.3	8.3	5.8	41.6	3353

† Relative scale on recorder paper running from 0 to 100.

‡ Counts/sec obtained from Geiger counter and timer circuit.

Table IV show a rough correlation of this type, the samples (5), (7) and (10) showing three of the four highest micropore volumes and the greatest decreases in specific area in going from the calcined cokes to the graphitized plates. Calcined coke samples (9) and (11) show no micropore volume and a small decrease in area.

It is not known whether a decrease in area in going from calcined coke to graphitized plate is, in part, a result of lower specific

area in the binder carbon. Apparently, however, addition of the binder, *per se*, has little effect on surface area since markedly different changes in surface area are found for the addition of the same binder content. It can be said that the surface area of the graphitized binder phase appears to be not too different than that of the coke. It is interesting, however, that upon reacting graphitized carbon bodies with an oxidizing gas, the rapid, initial increase in specific



area of the body is attributed primarily to increase in binder area<sup>5</sup>. This, along with the rapid increase in helium density upon small burn-offs of carbon bodies<sup>6</sup> does suggest that the binder phase contains an appreciable amount of area in closed micropores.

Table IV also presents data on pore volumes for the calcined cokes and graphitized plates. The total pore volume is arbitrarily defined as consisting of the sum of the volume which is open to helium penetration and that which is closed. This total pore volume is calculated from the difference of reciprocals of apparent and true densities. The total open-pore volume is calculated from the difference of the reciprocals of apparent and helium densities. The total closed-pore volume is the difference between the total and total open-pore volumes. The total open-pore volume can be divided into total open-micropore and total open-macropore volume, with the dividing line arbitrarily being a pore radius of 475 Å in the present paper.

The total pore volumes and total open-pore volumes of the graphitized plates are found to be greater than those of their calcined coke counterparts in every case. This is a result of the introduction of void volume between particles upon packing, as was discussed previously in conjunction with the apparent density data.

The total closed-pore volumes in the calcined cokes are found to be related to the intensity of their (002) X-ray diffraction peak, as shown in Fig. 3. Since the intensity of the (002) diffraction peak is in turn related to the number of layer planes orientating parallel to the X-ray slide, the conclusion is drawn that the closed-pore volume is primarily a result of random stacking of carbon crystallites, this random stacking producing closed voids. This correlation for the graphitized plate samples is not as good, probably because

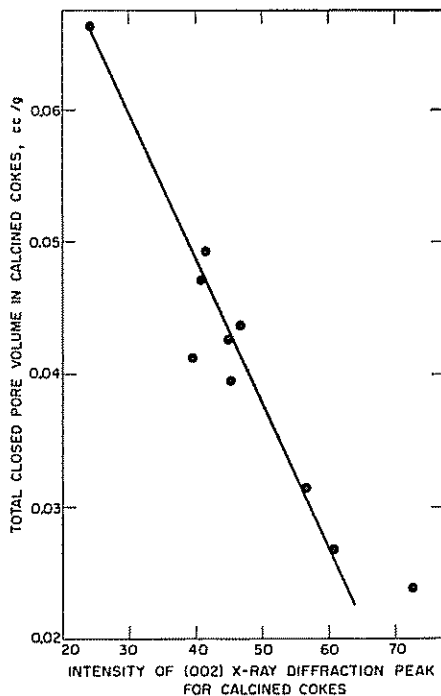


FIG. 3. Relation between intensity of (002) X-ray diffraction peak for calcined cokes and total closed-pore volume in cokes.

of the complications produced in averaging the effect in a two-phase system.

In going from the calcined cokes to the graphitized plates, some of the closed-pore volumes are found to increase while others decrease. This is the result of two counterbalancing factors—probable decrease of closed-pore volume in the coke upon graphitization and introduction of closed-pore volume in the binder. If the reduction in closed-pore volume in the coke is marked, a decrease in total closed-pore volume would be expected. On the other hand, a small decrease in closed-pore volume in the coke would result in an overall increase in closed-pore volume in the carbon plate.

It is seen that there is substantial increase in total open-macropore volume in going from calcined cokes to graphitized plates. This is a result of the introduction of voids between coke particles on packing, as shown

<sup>5</sup> C. N. Spalaris, *J. Phys. Chem.* **60**, 1480 (1956).

<sup>6</sup> E. M. Dresel and L. E. J. Roberts, *Nature, Lond.* **171**, 170 (1953).

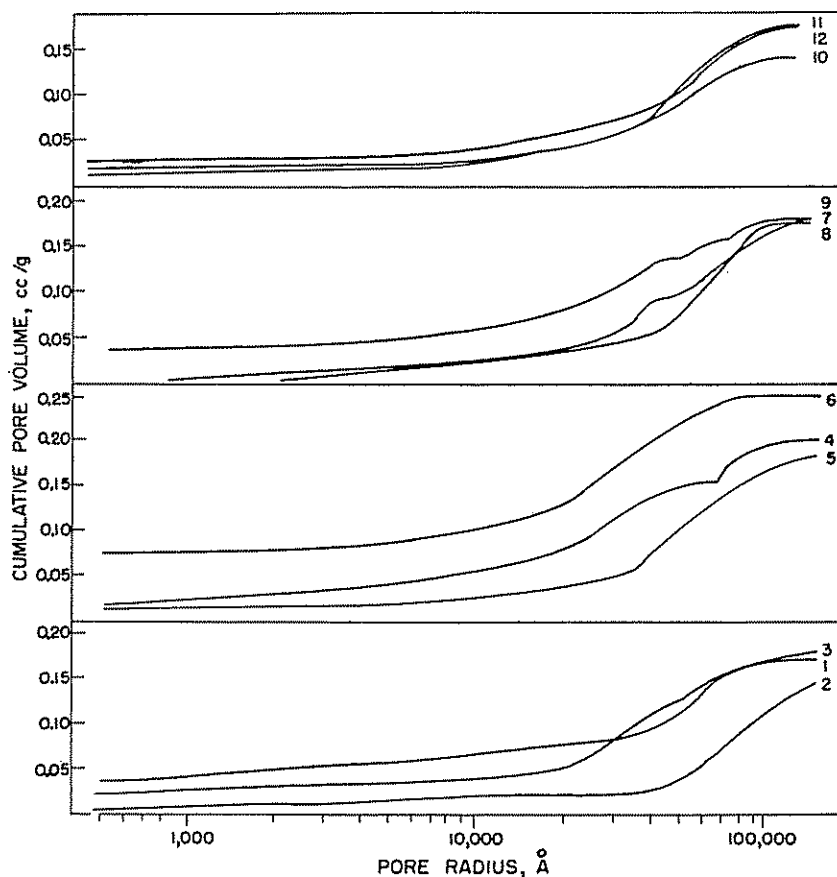


Fig. 4. Macropore-volume distributions for graphitized carbon plates as determined by the mercury porosimeter.

in Fig. 4, where the macropore-volume distributions for the graphitized plates are presented. The accumulation of a large pore volume in the pore radius range  $3\text{--}10\mu$  is characteristic of similar findings on commercial samples of baked and graphitized carbon bodies<sup>3</sup>.

It is noted that the macropore volume between  $10$  and  $15\mu$  radius is unusually large for sample (2), which has the coal tar pitch coke as the filler material. Three explanations appear possible. The pitch binder more completely entered the pores of the coke particles and left a greater average pore radius in the voids between particles, the particles of coke grew somewhat on graphitization resulting in larger voids upon its being

packed, or the number of fine particles in this coke was less. The first suggestion would not seem to account for the result, since the coking value of the binder in this sample was low (Table II) which, from Fig. 1, would suggest that a minimum of pitch went into the pores. At this point, there is little to choose between explanations (2) and (3). As seen in Fig. 4, plate 4, and plates 7 and 9 to a lesser extent, show a bi-modal distribution of macropore volume, which has previously been reported on commercial samples and is a result of a bi-modal distribution of fine particle-sized material<sup>3</sup>.

Also listed in Table IV are total open-micropore volumes in the calcined cokes and graphitized carbon plates. As has been

previously discussed<sup>3</sup>, these volumes are too high by the magnitude of macropore volume blocked by micropore constrictions below 475 Å in radius. Some idea of the amount of macroporosity trapped in this manner can be obtained by summing up the incremental surface area over the macropore distribution range and comparing it with the *BET* area<sup>3</sup>. If the summed area is higher than the *BET* area, a significant volume of trapped macroporosity is indicated. This has not been done for the curves shown in Fig. 4.

It is seen that the amount of microporosity in going from the calcined cokes to the graphitized plates increases, in some cases, and decreases in others. This depends upon the amount of microporosity in the coke which is blocked by binder relative to the amount of new microporosity introduced in the binder phase.

Open microporosity in the total porosity, closed pore volume in the total pore volume, and closed pore volume in the total sample volume, all expressed in per cent, are also included in Table IV.

Intensities of the (002) X-ray diffraction peak of the calcined cokes and graphitized carbon plates are included in Table IV. As discussed previously, this intensity is indicative of the orientation tendency of the carbon

particles and their crystallites. The relative intensities of the (002) peak for the carbon from the graphitized plates should qualitatively parallel the degree of orientation of crystallites perpendicular to the molding direction in the plates. This fact will be used presently in correlating properties of the graphitized plates.

From Fig. 5, it is seen that there is a qualitative correlation between the (002) peak intensities of the calcined cokes and carbon from the graphitized carbon plates. This again emphasizes the extreme importance of the raw material, calcined coke, in affecting properties of final carbon bodies.

#### E. Gas Reactivities, Coefficients of Thermal Expansion, Electrical Resistivities, and Transverse Breaking Strengths of Graphitized Carbon Plates

Probably the four most important properties of baked and graphitized carbon bodies are gas reactivity, coefficient of thermal expansion, electrical resistivity, and strength. Almost without exception, it is desired that a carbon body have a low rate of reactivity to gases, a low coefficient of thermal expansion, a low electrical resistivity, and a high strength. Probably the most critical of these properties, particularly for relatively high temperature applications, is the reactivity of carbon to gases. Carbon burn-off very rapidly increases the electrical resistivity and decreases the strength of the body to a point where it is unusable. The coefficient of thermal expansion is particularly important where the carbon body is exposed to a large thermal gradient and/or a rapid increase in temperature, since the higher the gradient and/or the increase in temperature, the more likely the body is to disintegrate. Electrical resistivity is particularly important in electrodes where it is desirable to carry a maximum current at minimum voltage. The parallel of electrical resistivity, thermal resistivity, is particularly important when carbon is used in heat exchangers and in

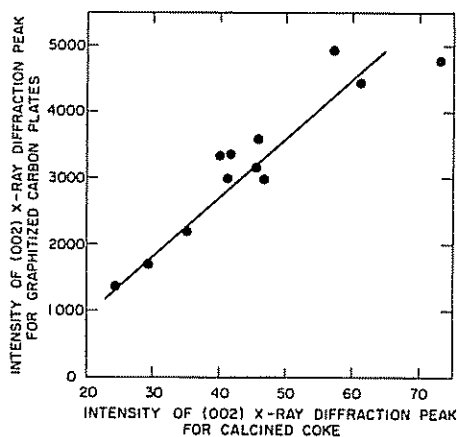


Fig. 5. Relation between (002) X-ray diffraction peaks for calcined cokes and the carbons from the graphitized plate counterparts.

moderators. Strength of the carbon body is particularly important where it is to be used as a structural material. It is to be emphasized that the properties of carbon bodies are usually highly anisotropic; and, as will be shown, it is of extreme importance to consider the most desirable orientation of particles within the body to obtain the optimum performance from the body under given conditions.

TABLE V  
*Gas Reactivities, Coefficients of Thermal Expansion, Electrical Resistivities, and Transverse Breaking Strengths of Graphitized Carbon Plates*

Sample	Gas reactivities (g/hr)	C T E ( $^{\circ}\text{C}^{-1} \times 10^3$ )	Electrical resistivities ( $\Omega\text{cm} \times 10^3$ )	Transverse breaking strength (lb/in <sup>2</sup> )
(1)	0.21	3.9	235	2028
(2)	0.88	4.5	138	2520
(3)	0.70	2.6	131	1300
(4)	0.68	2.8	126	1552
(5)	0.76	3.3	125	1570
(6)	0.65	2.7	138	1533
(7)	0.67	2.8	118	1312
(8)	0.41	2.6	119	1158
(9)	0.47	2.9	138	1337
(10)	0.90	6.1	151	2360
(11)	0.28	1.9	114	1730
(12)	0.68	2.8	138	1458

Table V presents the data on the four properties discussed above for the graphitized carbon plates. Reaction rates as a function of time were determined up to burn-offs of 40% on all samples. Typical curves<sup>1, 7</sup>, showing an increasing reaction rate up to ca. 5% burn-off and then a constant rate up to ca. 35% burn-off when expressed as grams per hour reacting at 1000°C, were found. First, from Table V, it is seen that different cokes have a markedly different effect on the reactivity of their graphitized carbon plate counterparts. This variation in reactivity is thought to be primarily due to a variation in the percentage of the surface of the coke particles (and their graphitized product) which is composed of crystallite basal planes.

<sup>7</sup> P. L. Walker, Jr. and E. Raats, *J. Phys. Chem.* **60**, 364 (1956).

Smith and Polley<sup>8</sup> have shown that a graphitized carbon black, where the surface is completely composed of basal plane structure, has an unusually low reactivity to air; and, on the other hand, the original carbon black, even though of essentially the same particle size and low internal porosity, has a strikingly higher reactivity, because a higher percentage of its surface is composed of crystallite edges instead of basal planes.

A good indication of the relative amount of basal plane structure in the surface of a carbon particle can usually be obtained by observing the tendency of this particle to orient when deposited on a backing slide—intensity of the (002) X-ray diffraction peak being used as a criterion of this, for example. This is true since the degree of orientation of the carbon particle is primarily affected by the shape of the particle, which in turn is affected by the orientation of crystallites composing the particle. Random crystallite arrangement results in the production of particles of essentially symmetrical shape upon grinding; whereas, crystallite orientation results in particles of unsymmetrical shape (long and flat), the degree of non-symmetry depending upon the extent of orientation.

The greater the intensity of the (002) X-ray diffraction peak for the carbon from the graphitized plate, the greater is the fraction of the surface of the plates which should be composed of crystallite basal planes. In Fig. 6, the intensity of the (002) X-ray diffraction peak for the graphitized carbon plates is plotted versus the reactivity of the plates; and a qualitative correlation is obtained, confirming the importance of basal plane orientation on the surface of the plate.

Sample (1) is a marked exception to even the qualitative correlation with its low reactivity and low (002) X-ray diffraction intensity. Its result presents another consideration of major importance. Sample (1)

<sup>8</sup> W. R. Smith and M. H. Polley, *J. Phys. Chem.* **60**, 689 (1956).

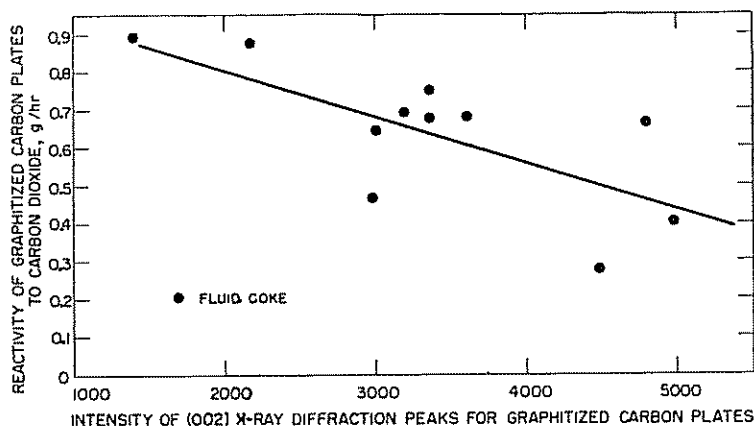


Fig. 6. Relation between the intensity of  $(002)$  X-ray diffraction peak for carbon from graphitized carbon plates and reactivity of the plates to carbon dioxide.

is composed of the fluid coke. The fluid coke particles are actually spherical in shape and upon graphitization, would be expected to form a particle the surface of which is composed of pentagonal and hexagonal faces, as discussed by Kmetko<sup>10</sup> in the case of carbon blacks. This means that the surface of the graphitized fluid coke can be expected to consist of basal plane structure almost entirely, which would result in this material having a low reactivity in analogy with the findings of Smith and Polley<sup>8</sup>.

It is seen then, that to produce carbon bodies of minimum reactivity to oxidizing gases, the graphitized coke particles should ideally be of either of the two structures presented in Fig. 7. Structure A is the ideal material which would be strived for when conventional cokes are used as raw materials, and structure B is the ideal material when carbon blacks or fluid cokes are the raw materials. Structure A represents a particle which is composed of one carbon crystallite (a single crystal). Obviously, even for this particle, reactivity along the  $c$ -dimension will be high; and, therefore, it is desirable to have the  $c$  to  $a$  ratio approach zero in the



Fig. 7. Ideal structures of graphitized coke particles for the production of carbon bodies of low gas reactivity.

limit. Structure B is a polyhedron, with reaction to oxidizing gases being primarily confined to points where the basal-plane faces join. Probably in practice it is easier to

<sup>10</sup> E. A. Kmetko, *Proc. 1st and 2nd Carbon Conf. University of Buffalo* (1956), p. 21.

realize a greater percentage of basal plane structure in the surface of particle B than particle A. Carbon from bodies composed of structure A plus a binder would produce the ultimate in intensity of the (002) X-ray diffraction peak; whereas, carbon from bodies composed of structure B plus a binder would produce the lowest (002) X-ray diffraction intensity. Furthermore, the experimental ratio of intensities for the (002) and (100)

their reactivity. As far as a correlation with specific surface area of the plates is concerned, it is seen that the area of sample (1) is close to the maximum area found and yet its reactivity is the lowest; sample (2) has the lowest surface area and yet the second highest reactivity found.

The ideal structure of graphitized coke particles insofar as producing a carbon of low gas reactivity is concerned, is not necessarily

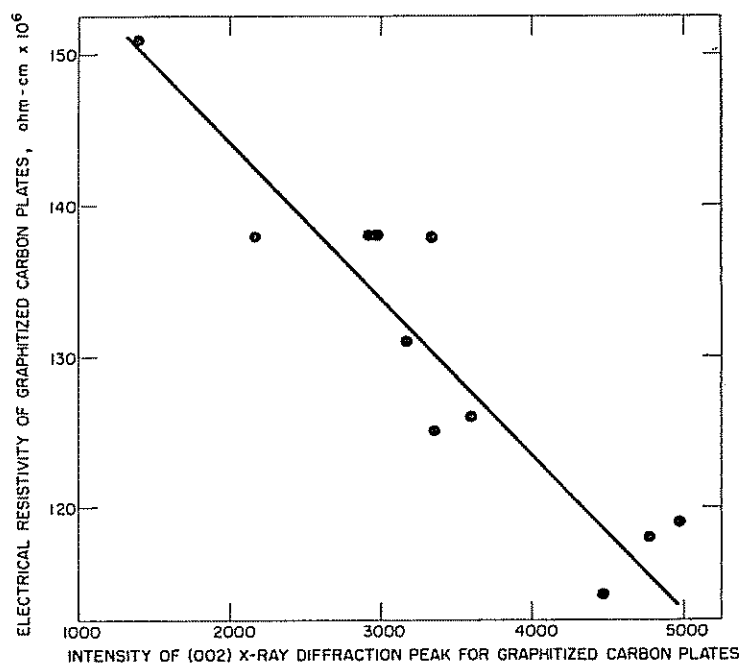


Fig. 8. Relation between intensity of (002) X-ray diffraction peak for graphitized carbon plates and their electrical resistivities.

diffraction peaks should be considerably greater than the theoretical ratio, based on structure factor considerations, for carbon from bodies composed of structure A and essentially in agreement for bodies composed of structure B<sup>1</sup>.

It is also appreciated that other properties of carbon bodies such as mineral impurity content, porosity, and surface area may play a part in determining reactivity. In the present work, however, there appears to be little relation between the ash content or porosity of the graphitized plate samples and

the ideal body when other important properties are considered. Bodies composed of filler of structure B would be expected to have a higher electrical resistivity in the direction perpendicular to molding pressure than bodies composed of structure A. This is shown to be the case by comparing the resistivity of sample (1) with those of other samples in Table V. Disregarding sample (1) because of its very high resistivity, the electrical resistivities of the graphitized plates are plotted against the intensity of their (002) X-ray diffraction peak in Fig. 8. It is seen

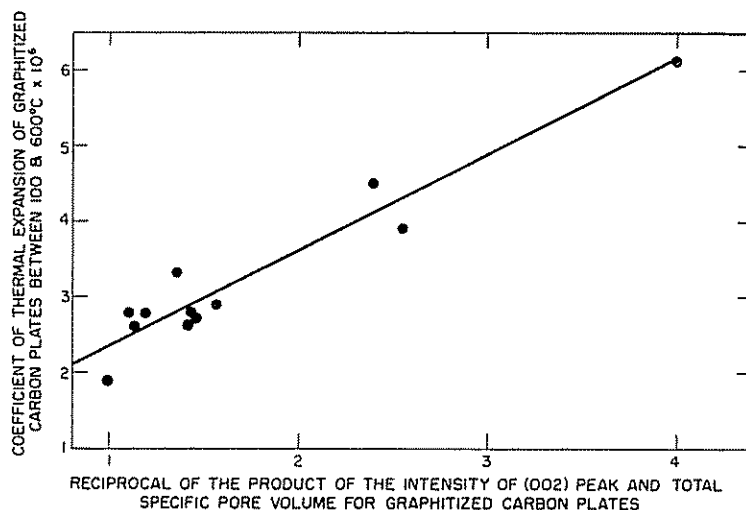


FIG. 9. Relationship between the reciprocal of the product of the intensity of the (002) peak and total specific pore volume for graphitized carbon plates and their coefficients of thermal expansion.

that a qualitative correlation exists, in spite of the variations in porosity and surface area of the plates, which should affect the results. This correlation is readily understandable since the resistance to current flow along the basal plane of carbon is considerably less than across the basal plane. Thus, the greater the orientation of basal planes parallel to the direction of current flow, the lower the electrical resistivity should be, all other factors equal.

The coefficient of thermal expansion of carbon bodies perpendicular to the molding direction should be inversely proportional to both the extent of basal plane orientation in this direction and to the total pore volume in the body. Figure 9 presents the data for the coefficient of thermal expansion versus the reciprocal of the product of the (002) X-ray diffraction peak and total specific pore volume for the graphitized carbon plates. A good qualitative correlation of the data is obtained,

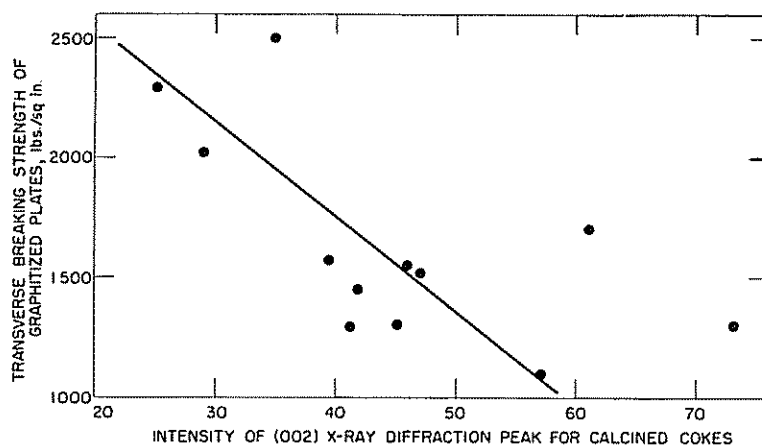


FIG. 10. Relation between intensity of (002) X-ray diffraction peak for calcined cokes and transverse breaking strength of their graphitized plate counterparts.

which explains the results for coefficient of thermal expansion.

From Fig. 10, it is seen that the nature of the coke has a marked effect on the transverse breaking strength of the graphitized coke body. According to Mrozowski<sup>11</sup>, when a carbon body yields under stress, a process of yielding has to occur in the binder bridges because here the stresses are the highest. Nevertheless, a general correlation of the strength-results obtained in this work shows that the calcined cokes, having the highest degree of disorder in their crystallite arrangement (samples (1), (2) and (10)), produce final graphitized carbon bodies of the highest strength. This fact can be a result of the high inherent strength which such filler material gives to the body and/or the effect which different fillers have on the interaction of the coke with the binder phase. According to Mrozowski<sup>11</sup>, for high strength the binder does much more good when it is between particles serving as bridge material than within the pores of the particles (or, according to Mrozowski, the strength is affected by interaction of the two materials). If interaction were playing a part in the present case, it would be expected that calcined cokes of the lowest pore volume, which would thereby be expected to permit the smallest pitch penetration into their pores, would produce the highest strength in the graphitized plates. Such is found to be qualitatively the case, with calcined coke sample (10) having the lowest total pore

volume (of those samples reported) and the highest strength. However, on many of the other samples, no systematic relationship on this point is found.

#### IV. CONCLUSIONS

Different calcined cokes are found to have a marked effect on the properties of their graphitized plate counterparts. Probably the most important property of the cokes found in affecting subsequent gas reactivity is the fraction of the surface of the coke particle which exposes crystallite basal planes. A high percentage of basal planes in the surface of the coke particles results in a low reactivity of the graphitized plates produced therefrom. Ability to orient the coke particles so that the maximum percentage of basal planes lie parallel to the direction of current flow is found to produce a minimum electrical resistivity. The reciprocal of the product of the tendency for the coke particles to orient with their basal planes parallel to the measuring direction and  $\bar{r}$  total pore volume of the graphitized plates is found to correlate with the coefficient of thermal expansion data for the graphitized plates. The strength of the graphitized plates is found to be affected by the coke used. The greater the degree of disorder of crystallite arrangement in the calcined coke, the greater the strength produced in the graphitized plate. It is, therefore, seen that many of the important properties of graphitized (and baked) carbon bodies can be predicted (on a relative basis) in advance, from the properties of their calcined coke counterparts discussed herein.

<sup>11</sup> S. Mrozowski, *Proc. 1st and 2nd Carbon Conf.*, University of Buffalo (1956), p. 195.