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Anthracite Electrodes

COMPARISON OF PROPERTIES OF CARBON AND GRAPHITE BODIES PRODUCED FROM ANTHRACITE AND PETROLEUM COKE†

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The effect of using anthracite as a substitute filler material for petroleum coke in the manufacture of baked and graphitized bodies was studied. Bodies were prepared from two anthracites and a fairly typical petroleum coke, each of which was mixed with an equal proportion of the same coal-tar-pitch binder and extruded in $\frac{1}{2}$ in. diameter rods. All of these rods were baked to 900°C, and part of them were further graphitized in a helium atmosphere to 2400 and 2800°C. A number of physical and chemical properties of the rods were studied and compared. At both graphitization temperatures, the bodies fabricated from the anthracites had (1) electrical resistivities at least 70% greater than those of the bodies fabricated from the petroleum coke, (2) lower apparent densities, (3) higher specific surface areas, (4) higher ash contents, (5) higher transverse breaking strengths, (6) smaller crystallite sizes, (7) less crystallite alignment, (8) larger interlayer spacings, and (9) mixed reactivity results with CO₂. For the baked bodies, differences in properties (1) and (6) were less marked and differences in properties (2), (3), (4), and (5) were more marked.

I. INTRODUCTION

Anthracite is currently being utilized to some extent as a filler in the manufacture of electrodes and pot liners for various electrolytic and electrothermal processes. It is known from experience that the properties of bodies produced from anthracite are generally significantly different from those for bodies produced from petroleum cokes. Although studies have been conducted on the strength of anthracite-pitch bodies¹ and on the degree of graphitization of anthracite², no significant contributions have appeared in the literature, which attempt to explain why the properties of anthracite bodies are different from those of petroleum coke bodies. The purpose of this investigation,

therefore, was twofold: first, to determine and compare the physical structure of anthracite and petroleum coke bodies and, second, to relate this structure to their gas reactivities, electrical resistivities, and mechanical strength. Among the properties to be investigated, to delineate clearly physical structure, were detailed pore size distributions obtained from mercury porosimeter data, densities measured in various media, surface areas from low temperature gas adsorption, and interlayer spacings and crystallite dimensions of the carbons from X-ray diffraction studies.

Bodies for the program were prepared from two anthracites, A-1 and A-2, and from a petroleum coke, P.C., currently being used in commercial production of graphitized electrodes. The proximate analyses of the raw anthracites and the green petroleum coke are shown in Table I.

† Based on a Ph.D. thesis submitted by I. Geller to the Graduate School of The Pennsylvania State University, September 1958. This research was supported by the Commonwealth of Pennsylvania.

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¹ D. W. Gillmore, C. C. Wright, and C. R. Kinney, *J. Inst. Fuel* **32**, 50 (1959).

² M. G. Boobar, C. C. Wright, and C. R. Kinney, *Ind. Eng. Chem.* **50**, 27 (1958).

II. EXPERIMENTAL

A. Sample Preparation

The filler carbons were first ground and calcined to approximately 1200°C in an

TABLE I

Proximate Analyses of Raw Anthracite and Green Petroleum Coke Flours

Sample	As received basis					Dry ash-free basis	
	F.C.	V.M.	H ₂ O	Ash	S	F.C.	V.M.
P.C.	88.5	11.0	0.3	0.2	1.5	88.9	11.1
A-1	86.6	2.9	3.4	7.1	0.5	96.7	3.3
A-2	82.9	5.9	2.7	8.5	0.7	93.4	6.6

inert atmosphere. Additional grinding was carried out after calcination until the particle sizes of the three materials were similar. The flours consisted of about 28% of -325 mesh material, with all the flour less than 48 mesh. The carbons were then mixed with coal-tar pitch (melting-point 100°C; benzene insoluble, 30.3%; quinoline insoluble, 12.7%) for 1 hr at 132°C. Forty parts of pitch to 100 parts of filler were used in each case. After mixing, the paste was molded into slugs 4 in. in diameter and 1 ft long under a pressure of 6000 psi. The slugs were then fed, without cooling, into a Watson-Stillman horizontal press and extruded through a 0.6 in. diameter die, the temperature of which was maintained at 136°C. For slugs containing petroleum coke, an extrusion pressure of *ca.* 7000 psi was used, whereas for the slugs containing anthracite a pressure of *ca.* 34,000 psi was required.

Baking and graphitizing were carried out on 1-ft long sections of the three materials during the same furnace runs. All of the rods were baked to 900°C on a "slow schedule" in a muffle furnace, after which some were heated to either 2400 or 2800°C in a tube furnace swept with He at 1 atm. In order to determine the effect of heat treatment on the filler material alone, 1 kg of each filler was also heated to 2800°C. The heating-up periods to 2400 and 2800°C were 1.5 hr and 2.5 hr, respectively. Soak time at maximum temperature was 1.5 hr.

B. *Methods and Apparatus for Sample Testing*
Samples of appropriate length and

diameter were cut from the 1-ft long rods for various tests as they were needed.

1. *Reaction rate studies.* The reaction rate apparatus used was essentially the same as that described by Walker, Foresti, and Wright³, with modifications in the balance and temperature control system. Two-inch long samples were reacted with CO₂, the reaction rates being determined from weight loss measurements.

2. *Transverse breaking strengths.* Transverse breaking strengths were determined by a Dillon fiber stress tester, which measured the pressure necessary to snap a rod sample mounted on two triangular wedges 3 in. apart. Stress was applied by a third wedge resting on the top of the sample midway between the supporting wedges.

3. *Gas adsorption.* A standard low-temperature gas adsorption apparatus was used to measure surface areas with N₂ at 78°K. The areas were calculated by the BET method⁴.

4. *Resistivities.* Electrical resistivities were obtained on both rod and particle samples by comparing the potential drop across a fixed resistance with that across the sample. The details of the technique have been reported elsewhere⁵.

5. *Porosimeter studies.* The mercury porosimeter used has been described⁶. With

³ P. L. Walker, Jr., R. J. Foresti, Jr., and C. C. Wright, *Ind. Eng. Chem.* **45**, 1703 (1953).

⁴ S. Brunauer, P. H. Emmett, and E. Teller, *J. Amer. Chem. Soc.* **60**, 309 (1938).

⁵ P. L. Walker, Jr. and F. Rusinko, Jr., *Fuel* **36**, 43 (1957).

⁶ P. L. Walker, Jr., F. Rusinko, Jr., and E. Raats, *J. Phys. Chem.* **59**, 245 (1955).

this apparatus, it was possible to determine the pore size distribution of the sample between pore radii of 71 and 160,000 Å.

6. *X-ray diffraction studies.* Standard X-ray diffraction procedures were used to calculate average interlayer spacings and crystallite heights for both the baked and graphitized rods and flours⁷. Sodium chloride was employed as an internal standard with the graphitized carbons.

7. *Density measurements.* Bulk densities were determined on all rod samples by dividing the weight of the rod by its geometric volume. Helium densities were determined in a thermostated, constant pressure, null type apparatus. X-ray densities were calculated on all samples from their *d*-spacings in the standard manner. The C—C bond distance within the layer plane was taken as 1.42 Å.

8. *Proximate analyses.* Proximate analyses were determined according to A.S.T.M. procedures⁸.

III. RESULTS AND DISCUSSION

A. Weight and Volume Changes in Rods with Heat Treatment

Weight and volume changes were measured following heat treatment, as shown in Tables II and III. These data represent averages of

TABLE II

Body Weight Losses During Heat Treatment

	Weight loss, %		
	P.C.	A-1	A-2
Extruded to baked	12.3	11.2	10.0
Baked to 2400°C	2.9	9.9	12.9
Baked to 2800°C	3.4	10.5	13.4

⁷ P. L. Walker, Jr., H. A. McKinstry, and J. V. Pustinger, *Ind. Eng. Chem.* **46**, 1651 (1954).

⁸ American Society for Testing Materials, Procedure D 271-48, A.S.T.M. Standards on Coal and Coke (1954), pp. 9-39.

TABLE III

Volume Changes of Bodies During Heat Treatment

	Volume change, %		
	P.C.	A-1	A-2
Extruded to baked	-2.3	-2.5	-1.6
Baked to 2400°C	+0.2	-8.0	-8.9
Baked to 2800°C	nil	-8.4	-11.7

20 rods each for the baked samples and 10 rods each for the graphitized samples. Weight losses incurred during baking are similar for all three materials and can be attributed mainly to the coking of the binder. Weight losses during graphitization are considerably higher for the anthracites than for the petroleum coke, because of volatilization of the mineral matter.

The three bodies undergo roughly the same amount of shrinkage upon baking. However, upon graphitization of the baked materials, the two anthracite bodies undergo an additional, substantial shrinkage, whereas the petroleum coke body undergoes negligible volume change. This is attributed to the affect of temperature on the density of the filler. That is, the petroleum coke undergoes little density change upon graphitization, whereas the anthracites undergo considerable density increase.

B. Crystallographic Changes in Rods and Flours with Heat Treatment

Table IV summarizes the results for interlayer spacing, crystallite diameter, and intensity of the (002) diffraction peak for all the samples. The interlayer spacings of the petroleum coke flour and bodies are significantly less than those of the anthracite samples, following heat treatment to 2400 or 2800°C, indicating clearly the greater graphitizability of the petroleum coke. Crystallite heights of the graphitized petroleum coke

TABLE IV

Crystallographic Changes in Rods and Flours with Heat Treatment

Sample	Heat treatment temp., °C	d-spacing, Å	\bar{L}_c , Å	Relative intensities†
<i>Raw flours</i>	None			
P.C.		3.51	25	34
A-1		3.51	14	19
A-2		3.51	14	20
<i>Calcined flours</i>	1200			
P.C.		3.45	33	100
A-1		3.49	14	25
A-2		3.45	16	26
<i>Graphitized flours</i>	2800			
P.C.		3.361	898	100
A-1		3.371	330	40
A-2		3.366	506	69
<i>Baked rods</i>	900			
P.C.		3.45	32	85
A-1		3.49	15	25
A-2		3.45	14	24
<i>Graphitized rods</i>	2400			
P.C.		3.373	728	52
A-1		3.382	199	14
A-2		3.381	208	19
<i>Graphitized rods</i>	2800			
P.C.		3.364	844	60
A-1		3.380	208	21
A-2		3.375	282	31

† Relative intensities of both the non-graphitized and graphitized samples are expressed on the basis of 100. Relative intensities between the two groups have no significance.

samples are significantly greater than those of the anthracites. As discussed previously⁹, the intensity of the (002) diffraction peak can be taken as an indication of the relative extent of crystallite alignment. Clearly, the crystallite alignment in the petroleum coke samples, for any heat treatment temperature, is greater than that in the anthracites. Indeed, the better crystallite alignment in the calcined petroleum coke probably is responsible for its greater graphitizability.

C. Mechanical Strength of Electrodes

The strength results, listed in Table V, show that samples prepared from both anthracites were stronger than those prepared from petroleum coke and that the A-2 rods

were stronger than the A-1 rods. It is important, however, to recognize the possible effect of extrusion pressure on these results. The anthracite pastes required almost five times as much pressure for extrusion as did the petroleum coke paste.

D. Mineral Impurities

Also shown in Table V is the effect of heat treatment on the mineral matter content of the flour and rod samples. The mineral matter content of the calcined anthracite flours and the baked anthracite rods is high. Essentially none of the mineral impurities was removed by calcination or baking. Upon heat treatment to 2400 and 2800°C, substantial removal of mineral matter from the anthracite samples occurs. However, for a soak time of only 1.5 hr at maximum temperature, the mineral matter remaining

⁹ P. L. Walker, Jr., F. Rusinko, Jr., J. F. Rakaszawski, and L. M. Liggett, *Proc. Third Carbon Conf.*, Pergamon Press (1959), p. 643.

TABLE V

Total Ash, Transverse Breaking Strengths, and Electrical Resistivities of Various Samples

Sample	Ash, %	Transverse breaking strength, psi	Resistivity, ohm-cm
<i>Calcined flours (1200°C)</i>			
P.C.	0.28	—	0.011†
A-1	7.75	—	0.032
A-2	9.24	—	0.030
<i>Graphitized flours (2800°C)</i>			
P.C.	nil	—	0.0028
A-1	0.60	—	0.0058
A-2	0.40	—	0.0053
<i>Baked rods (900°C)</i>			
P.C.	0.38	3800	0.0053
A-1	5.96	5000	0.0067
A-2	7.62	5600	0.0063
<i>Graphitized rods (2400°C)</i>			
P.C.	0.15	2900	0.0014
A-1	0.72	3900	0.0029
A-2	1.28	4200	0.0023
<i>Graphitized rods (2800°C)</i>			
P.C.	0.06	3300	0.0010
A-1	0.15	3700	0.0023
A-2	0.26	4300	0.0017

† Resistivities of powdered samples were measured at 10,000 psi.

n the anthracite is still considerably higher than that in the petroleum coke samples heat treated to comparable temperatures. Boobar and coworkers² have found that additional soak time produces a further decrease in the mineral matter content of anthracites.

The ash analyses reported are also strongly affected by heat treatment procedures. That is, a subsequent study indicated that when similar anthracite electrodes were heat-treated in a regular Acheson graphite furnace (at least to above 2400°C,) the ash content remained relatively high, approximately 25 to 30% of the starting value. In the experimental furnace, there was no coke packing around the rods and the volatilized impurities were swept away by a stream of He, which was used to maintain an inert atmosphere. On the other hand, in the Acheson furnace the rods were surrounded by a packing of coke to prevent oxidation and no gas was passed through the furnace. The escape

of mineral impurities in this latter case was obviously retarded.

E. Electrical Resistivities

Electrical resistivities were measured on all powder and rod samples. The results are listed in Table V. The graphitized petroleum coke rods have significantly lower electrical resistivities than the anthracite rods at comparable heat treatment conditions. As a matter of fact, the resistivity of the petroleum coke body following heat treatment to 2400°C is lower than that for the anthracite bodies heat treated to 2800°C. There is also a major difference in the resistivities of the two anthracite bodies.

The resistivities of the heat treated petroleum coke flours are also lower than those of the heat treated anthracite flours for comparable heat treatment temperatures. Resistivities of particulate materials, however, are affected by the number and nature of interparticle contacts. The true specific

resistance of the material within a particle is often masked by the contact resistance between particles. Very hard or rigid particles would not be expected to make as good contact with each other under selected pressures as particles of a softer, more pliable material, which could be more easily deformed. The resistances of the powder samples were measured at three different pressures, with the results being summarized in Table VI. Since the weight of the samples, the diameter of the container, and the height of the samples in the container at the different pressures were known, it was possible also to calculate the bulk densities of the samples at which the resistances were measured. The results are shown in Table VII.

TABLE VI
Variation in Electrical Resistivity of Particle Samples with Applied Pressure

Sample	Resistivity, ohm-cm		
	at 2500 psi	at 5000 psi	at 10,000 psi
<i>Calcined flours (1200°C)</i>			
P.C.	0.025	0.017	0.011
A-1	0.078	0.049	0.032
A-2	0.090	0.053	0.030
<i>Graphitized flours (2800°C)</i>			
P.C.	0.0045	0.0037	0.0028
A-1	0.013	0.0081	0.0058
A-2	0.0095	0.0070	0.0053

The bulk densities are affected by particle packing in the container, as well as by the particle densities. Plots of bulk density vs. resistivity, shown in Fig. 1 for the calcined flours and in Fig. 2 for the graphitized (2800°C) flours, are interesting. In both cases all values of resistivity are higher for the anthracites than for the petroleum cokes. However, it appears from the plots in Fig. 1 that if the curves for the calcined anthracites are extrapolated toward higher bulk densities, they will join the curve for the petroleum

TABLE VII

Variation in Bulk Densities of Particle Samples with Applied Pressure

Sample	Bulk density, g/cm ³		
	at 2500 psi	at 5000 psi	at 10,000 psi
<i>Calcined flours (1200°C)</i>			
P.C.	0.79	0.84	0.87
A-1	0.69	0.72	0.76
A-2	0.71	0.74	0.78
<i>Graphitized flours (2800°C)</i>			
P.C.	0.87	0.95	1.02
A-1	0.81	0.86	0.93
A-2	0.82	0.88	0.96

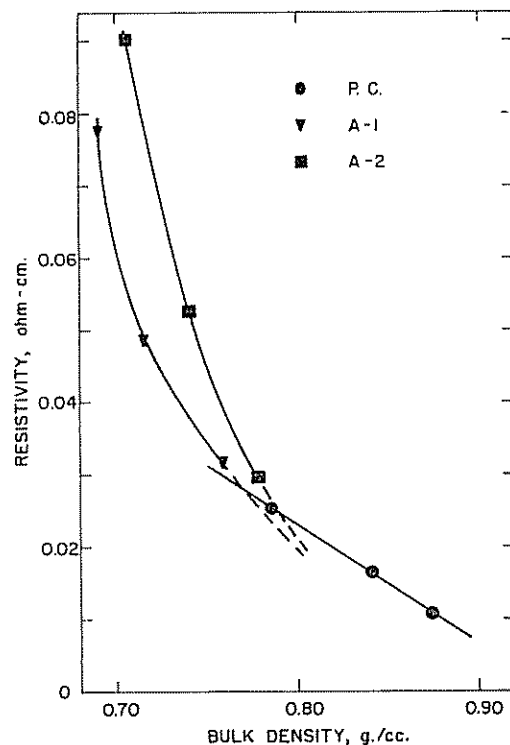


Fig. 1. Electrical resistivity as a function of bulk density for calcined flours.

coke, yielding similar resistivities for the same bulk densities. This is apparently not the case for the graphitized samples, where

the extrapolated curves for the anthracites do not approach the graphitized petroleum coke curve. These results, at least in part, explain the similarity of the resistivities of

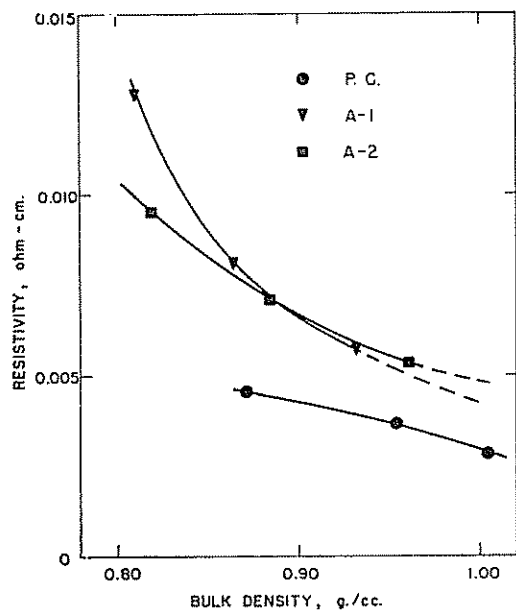


Fig. 2. Electrical resistivity as a function of bulk density for graphitized flours.

the baked rods (on the basis of percentage deviation) and the large differences in resistivities between the graphitized rods.

Comparing the resistivity data of Table V with the X-ray diffraction data in Table IV, it is apparent that the resistivities of the graphitized samples depend to an important extent on crystallite size and orientation; the larger the crystallite size and better the crystallite alignment the lower the resistivity. However, the resistivity differences between the baked anthracite and petroleum coke samples are not as marked as the X-ray data might lead one to expect. The presence of volatile matter on the crystallite edges can markedly affect the resistivity of baked carbons, however.

F. Pore Structure of Electrodes.

1. *Specific volumes and pore volumes.* X-ray, helium, and bulk densities were

determined on various samples. A correction was made for mineral matter using the equation¹⁰, $d = ad'(100 - A)/(100a - Ad')$, where d is the corrected density, d' is the uncorrected density, A is the % ash, and a is the density of the ash taken as 2.7 g/cm³. A summary of pore volume data is presented in Table VIII. The total pore volume was calculated as the difference between the reciprocals of the bulk and X-ray densities. The closed pore volume was calculated as the difference between the reciprocals of the helium and X-ray densities. The open pore volume is the difference between the total and closed pore volumes.

Included in Table VIII are the closed pore volumes of the binder. It was possible to calculate these volumes in the following way: Assuming that the closed pore volume in the mineral matter is negligible, the closed pore volume of the sample is equal to the sum of the closed pore volumes of its binder and filler. Since the ash-free weight of the sample is equal to the sum of the weights of filler and binder carbon, the closed pore volume of the binder, V_b , can be calculated from the equation, $V_b = V + (W_f(V - V_f)/W_b)$, where V is the closed pore volume of the entire sample per gram of sample, V_f is the closed pore volume of filler per gram of filler, W_f is the weight of filler in the sample, and W_b is the weight of binder in the sample. All samples were prepared in the ratio of 40 parts of pitch to 100 parts filler, and total weight losses during baking and graphitization were known. Assuming all weight loss in baking to be due to coking of the pitch, the weights of binder and filler in the baked rods could be calculated. Weight loss on graphitization was attributed to volatilization of mineral matter in the filler and additional loss of pitch constituents. Since the ash contents of the baked and graphitized rods were determined, weight loss due to volatilization of the mineral matter could be

¹⁰ A. M. Wandless and J. C. Macrae, *Fuel* **13**, 4 (1934).

TABLE VIII

Specific Pore Volumes for Flours and Electrodes

Carbon material	Pore volume, cm ³ /g								
	Total			Closed			Open		
	P.C.	A-1	A-2	P.C.	A-1	A-2	P.C.	A-1	A-2
Calcined flour	—	—	—	0.029	0.103	0.128	—	—	—
Graphitized flour	—	—	—	0.036	0.057	0.042	—	—	—
Baked rod	0.240	0.305	0.303	0.037	0.098	0.103	0.203	0.207	0.200
Graphitized rod (2400°C)	0.286	0.342	0.324	0.068	0.084	0.077	0.218	0.258	0.247
Graphitized rod (2800°C)	0.277	0.313	0.302	0.062	0.072	0.060	0.214	0.241	0.242
Binder of baked rod	—	—	—	0.075	0.079	0.014	—	—	—
Binder of 2800°C rod	—	—	—	0.202	0.159	0.154	—	—	—

calculated. Substantial amounts of closed pore volume are seen to be present in the binder fraction of the rods heat-treated to 2800°C.

2. *Pore size distributions.* A mercury porosimeter was employed to obtain pore size distribution curves for the baked and graphitized (2800°C) samples. The range of pore radii covered by the porosimeter data is from *ca.* 71 Å to about 160,000 Å. Figure 3

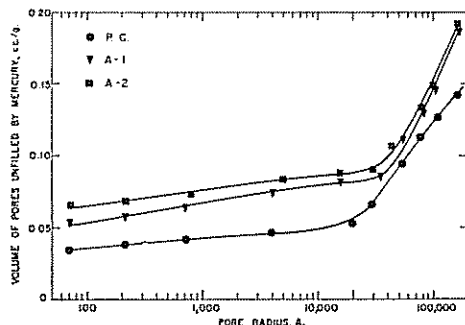


FIG. 3. Pore size distributions for baked rods.

presents porosimeter curves for the baked rods, while Fig. 4 shows curves for the graphitized rods. The resemblance of the curves for the three materials is striking, especially in the case of the baked samples.

3. *Surface areas.* It was not possible to reach equilibrium within a reasonable time with the baked anthracite rods for adsorption of N₂ at 78°K, but the drift was small after

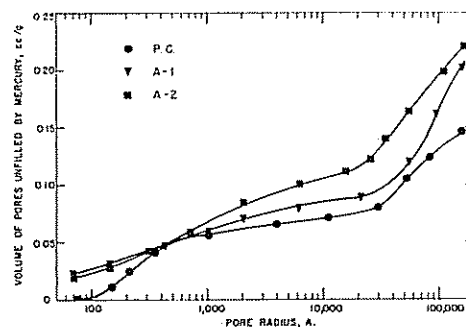


FIG. 4. Pore size distributions for graphitized rods.

about 20 min. Therefore, pressures were read arbitrarily after 30 min in all cases. After reaction of the rods with CO₂ to 10% weight loss at 950, 1000, and 1100°C, surface areas were again measured. A summary of all data appears in Table IX.

Column three of Table IX lists the surface areas calculated from pore size distribution data. These areas were calculated using an

TABLE IX

Surface Areas of Electrodes Before and After Reaction with CO₂

Sample	Surface area, m ² /g				
	Before reaction		After reaction (by N ₂ adsorption)		
	From N ₂ adsorption	From pore size distribution data	at 950°C	at 1000°C	at 1100°C
<i>Baked rods (900°C)</i>					
P.C.	0.4	17.1	38.5	28.4	12.6
A-1	10.4	27.0	51.4	41.0	26.5
A-2	10.7	32.9	51.8	40.3	26.9
<i>Graphitized rods (2400°C)</i>					
P.C.	0.4	—	1.7	2.3	3.8
A-1	2.0	—	12.9	12.3	16.3
A-2	2.4	—	11.1	16.1	22.0
<i>Graphitized rods (2800°C)</i>					
P.C.	0.4	3.9	1.4	2.1	3.5
A-1	2.3	11.4	13.4	14.6	18.9
A-2	2.1	10.5	13.7	17.8	18.0

equation¹¹ for cylindrical pores, $A = 2V/\bar{r}$, where A is the pore surface area, V is the pore volume, and \bar{r} is the average pore radius. For the purpose of calculation, the porosimeter curves were divided into volume increments over which the slopes of the curves were nearly constant. Average pore radii were calculated for these increments. An average pore radius of 40 Å was assumed for the volume of pores below 71 Å in radius. The sum of the areas calculated for each volume increment was taken as the surface area of the sample.

G. Significance of Changes in Pore Structure During Heat Treatment

1. *Bubble structure of the binder.* During the mixing process, the particles of filler material are coated with a layer of fluid binder, which solidifies on cooling and holds the entire mass in a rigid shape. When the rods are baked under proper conditions, the binder is coked slowly and decomposes; the volatile material is evolved in the gaseous

state and a highly carbonaceous skeleton is left behind.

Walker and co-workers⁹, among others, have reported the presence of two closed pore systems in rod or plate samples, one due to the voids between crystallites in the filler and the other in the binder. Walker and Raats¹² and Mrozowski^{13,14} suggested that the closed porosity in the binder is due to a bubble structure formed during the baking process. A thorough search of the literature, however, has revealed nothing concerning the changes occurring in this bubble structure on graphitization. Presumably, it should decrease, because of shrinking and cracking which is thought to take place at high temperatures. Actually the closed pore volume of the binder increases on graphitization with all three materials, as seen from Table VIII. It is difficult to postulate a mechanism for this, since the binder should be plastic only during baking.

¹² P. L. Walker, Jr. and E. Raats, *J. Phys. Chem.* **60**, 364 (1956).

¹³ S. Mrozowski, *Proc. 1st and 2nd Carbon Conf.*, University of Buffalo (1956), p. 31.

¹⁴ *Ibid.*, p. 195.

¹¹ P. H. Emmett and T. W. de Witt, *J. Amer. Chem. Soc.* **65**, 1253 (1943).

2. *Surface area development upon gasification.* One of the interesting results of this work is the apparently anomalous surface area development data obtained for electrodes upon gasification. From Table IX it is seen that surface area development, with increasing reaction temperature, decreases for the baked samples and increases for the graphitized samples. This behavior can be explained by the preferential reaction of the carbon at the outer edges of the particles as reaction temperature is increased. Petersen¹⁵ and Walker and Raats¹² have shown that at low temperatures reaction occurs uniformly through the rod and through the particles of which it is composed. As reaction temperatures are increased, reaction takes place preferentially at the surface of the particles, that is, in the binder. If the reaction temperature is raised sufficiently, reaction takes place primarily on the surface of the rod.

In all of the baked rods there is an appreciable micropore structure, probably due to the disoriented layers of carbon in both the filler and the binder. At low reaction temperatures it is to be expected that the ratio of filler to binder which reacts would be at a maximum. As a result, there is a greater efficiency in opening up this pore volume and developing new surface area at low temperatures than at higher temperatures.

In the graphitized rods this micropore structure has been greatly reduced, especially in the petroleum coke rods; and an extensive closed pore volume appears in the binder. Consequently, at higher temperatures, when the binder reacts preferentially, more of this closed pore volume is opened up and the surface areas increase with increasing reaction temperatures.

The magnitude of the surface area developed upon gasification of the graphite rods is considerably lower than that developed on reaction of the baked rods. This suggests that the closed pore system in the binder of

the graphitized rods consists of pores of much larger diameter than those of the micropore system in the baked rods. It is possible that the bubble structure formed in the pitch on gas baking is expanded on graphitization mainly by the enlargement of pores present rather than by creation of new bubbles.

3. *Capillary constrictions.* Bond and Spencer¹⁶ made an extensive study of the pore structure of several carbons and coals and the effect of carbonization on this structure. The coals studied ranged in rank from lignite to anthracite. From measurements of surface area and density with a number of gases and liquids of varying molecular size, they concluded that the carbons consisted of fused hexagonal rings oriented in such a way as to give rise to a large internal porosity more or less closed off at the ends by capillary constrictions. They felt that these constrictions were made smaller by carbonization, but the total internal volume was not changed appreciably.

It is possible to draw the same conclusion from the present work regarding the constricted pore structure of the electrodes. From the data in Table IX it is seen that the surface areas calculated from pore size distributions are consistently higher than those obtained by gas adsorption. This is the result expected if pore constrictions are present, since from porosimeter measurements the entire volume of a capillary lying behind a pore constriction would be considered to have the same radius as the constricted portion. As a result, too much pore volume is ascribed to pores of smaller radius, and it is these pores which contribute most heavily to surface area.

Regarding the change in pore structure on graphitization, however, the data in Table IX show that it is not only the size of the constrictions which changes, as reported by Bond and Spencer, but apparently the entire pore becomes smaller. If the constrictions

¹⁵ E. E. Petersen, Ph.D. Thesis, The Pennsylvania State University (1953).

¹⁶ R. L. Bond and D. H. T. Spencer, Industrial Carbon Conference, London (1957), pp. 231-51.

had become smaller while the rest of the pore had remained the same size, one would expect a decrease in the nitrogen surface area with a corresponding increase in the calculated area. Actually both areas decrease. Bond and Spencer carbonized their samples to a maximum of only 1100°C, so one might expect no extensive changes to occur. The petroleum coke and anthracite electrodes, on the other hand, were graphitized at 2800°C, during which process very significant changes took place in the structure of the carbons as shown by the X-ray diffraction data.

H. Reactivities

Reaction rates of the rod samples with CO₂ were determined at 950, 1000, and 1100°C by measuring the weight loss of the carbons with time. Rates, taken from the straight line portions of the plots, were divided by the weights of the starting materials to give specific reaction rates on a per gram basis.

It is normally expected that the reactivities of graphitized materials will be lower than those of their baked counterparts, because of the rate-retarding effect of graphitization¹⁷ and the catalytic effect of impurities¹⁸. The reactivities for the A-1 rods graphitized at 2400°C, however, were considerably higher at all three reaction temperatures than the rates for the corresponding baked rods. Extra samples of the three carbons were heat treated in a graphitizing furnace to 1550 and 2000°C. These samples were reacted at 1000 and 1100°C. A plot of reaction rate vs. heat treatment temperature is shown in Fig. 5 for samples reacted at 1000°C. The curves for samples reacted at 950 and 1100°C were of almost identical shape. It is apparent that the reactivities of the electrodes are not related in a simple way to the degree of

graphitization, the physical structure, or the amount or type of impurities in the samples. It is certain, however, that reactivity is dependent on all three of these parameters.

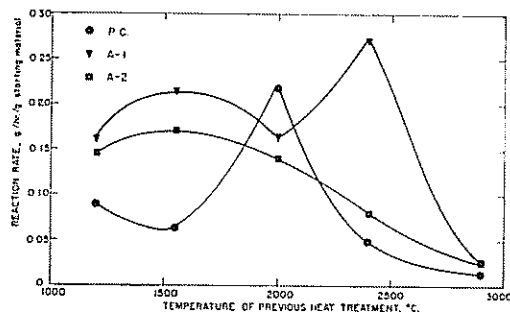


FIG. 5. Effect of heat treatment temperature on reaction rates with carbon dioxide at 1000°C.

It is probable, other factors being equal, that highly graphitic carbons are less reactive than baked carbons. However, although the crystallite sizes of the 2400°C graphitized anthracites are nearly the same and much smaller than the crystallite size of the 2400°C graphitized petroleum coke, the specific reaction rates of the A-2 and P.C. samples are alike, while that of the A-1 sample is much greater. Similar lack of correlation can be pointed out between reactivity and pore volume or impurity content of the samples. Other investigators^{19,20}, working with various carbons including petroleum cokes, pitch cokes, coal cokes, and anthracites, obtained similarly scattered data for reactivity of their samples with CO₂. In all cases the scattering was attributed to impurities. Walker and co-workers²⁰ found that the reactivity of a low-ash content coal-tar pitch coke to CO₂ increased significantly and went through a maximum on graphitization. This behavior is thought to be caused by the mineral impurities present in the coke breeze particles in the coal-tar pitch. Before graphitization,

¹⁷ W. D. Schaeffer, W. R. Smith, and M. H. Polley, *Ind. Eng. Chem.*, **45**, 1721 (1953).

¹⁸ F. J. Long and K. W. Sykes, *Proc. Roy. Soc. (London)* **A193**, 377 (1948).

¹⁹ Y. Kawana, *Bull. Chem. Soc. (Japan)* **27**, 334 (1954).

²⁰ P. L. Walker, Jr., C. R. Kinney, and D. O. Baumbach, *J. Chim. Phys.* **58**, 86 (1961).

the impurities are thought to be concentrated in that portion of the pitch coke, which originally was the coke breeze. Hence, their catalytic effect is localized and the observed reaction rate is low. Subsequent graphitization apparently promoted solid-state diffusion of the impurities, with the result that their catalytic efficiency was increased and the reaction rate increased. At about 2800°C, most of the impurities were removed by volatilization and the reaction rate decreased to a value below that of the ungraphitized sample. It is possible that a similar explanation can explain the present reactivity results. That is, heat treatment both disperses the mineral matter more uniformly through the carbon matrix and reduces its concentration. The predominating effect depends upon the heat treatment temperature.

IV. CONCLUSIONS

Baked and graphitized bodies have been fabricated using a typical petroleum coke

and two anthracites as fillers. A number of important properties of the bodies have been measured and compared. Differences in these properties have been explained in some cases on the basis of differences in physical properties of the bodies. In general, bodies produced from the anthracites used do not have as good properties as those produced from the petroleum coke. This is primarily attributed to a higher mineral matter content, smaller crystallite size, and poorer crystallite alignment in the anthracites. Differences in these properties were noted also for bodies made from the two anthracites examined. This suggests that anthracites may yet be found which impart properties to carbon bodies that approach the properties imparted by petroleum cokes, still more closely.

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