

## PROPERTIES OF MOLDED CEYLON NATURAL GRAPHITE\*†

FRANK RUSINKO, JR. and P. L. WALKER, JR.

Department of Fuel Technology, The Pennsylvania State University  
University Park, Pennsylvania

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Micron-sized Ceylon natural graphite (having an ash content of 2.1%) was molded into cylinders one inch long by  $\frac{1}{2}$  in. in diameter to apparent densities ranging from 1.61 to 1.99 g/cm<sup>3</sup>. Subsequently, molded samples were heat treated at temperatures between 1556 and 3017°C. The specific surface area of the powdered graphite decreased from 11.6 to 8.5 m<sup>2</sup>/g upon going from the original to the 2800°C heat treated material. Molding, even to a density of 1.99 g/cm<sup>3</sup>, resulted in a negligible decrease in the specific surface area, as measured by low-temperature gas adsorption. Heat treatment at a series of temperatures up to 3017°C resulted in a gradual decrease in the subsequent reactivity of the molded graphite to carbon dioxide. At a reaction temperature of 1000°C, the reactivity decreased from 1.32 g/hr for the original graphite to 0.048 g/hr for the material heat treated to 3017°C. For the original and 2600°C heat treated samples, reactivity to carbon dioxide was determined from 900 to 1100°C. Reactivities (g of carbon reacting/hour × atm. CO<sub>2</sub> × m<sup>2</sup> of carbon surface) were  $1.5 \times 10^5 e^{-42,000/RT}$  and  $1.7 \times 10^4 e^{-42,000/RT}$ , respectively. Additional properties of the molded samples which were determined include radial and longitudinal density distributions, hardness, crushing strength, macropore volume distribution, and electrical resistivity.

### I. INTRODUCTION

Some interest has been shown regarding the use of high density graphite as a moderating material in atomic reactors. In conventional carbon bodies composed of a filler and binder phase, high densities are frequently obtained by impregnating the body with a low melting point pitch, adding some small particle sized carbon black or lampblack to fill the voids between the larger petroleum coke particles, and/or baking under pressure to increase the coke yield of the binder phase. Another possibility of obtaining high density graphite bodies—that of compacting natural graphite under high pressures—has recently created interest. This process has some advantages over the more conventional methods used to attain high density. There is no mixing of the filler and binder phase and no relatively slow baking cycle. Further, a body of desired

density is obtained rather easily by varying the molding pressure and/or particle size distribution of the graphite. This paper summarizes some properties of bodies produced by the compaction of Ceylon natural graphite at pressures between 11,500 and 125,000 psi.

### II. EXPERIMENTAL

1. *Molding apparatus.* Ceylon natural graphite (Dixon's<sup>1</sup> type 200-10) was molded into rods  $\frac{1}{2}$  in. in diameter and slightly over 1 in. in length. A sketch of the mold used is shown in Fig. 1. The top 11 in. of the mold was cast iron; the bottom 4 in. was hardened steel. Two plungers were available, a longer one of cast iron used in the initial compaction at low pressures and a shorter one of hardened steel used in the final compaction at high pressures. It was found that cast iron could not be used for molding at pressures much above 25,000 psi without the plunger seizing in the mold.

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<sup>1</sup> The graphite was kindly supplied by S. B. Sealey of the Joseph Dixon Crucible Company, Jersey City, New Jersey.

Briefly, the procedure for making the samples was as follows: Between 6 and 8 g of graphite were poured into the mold (depending upon the final density desired) and compressed until all the graphite was in the

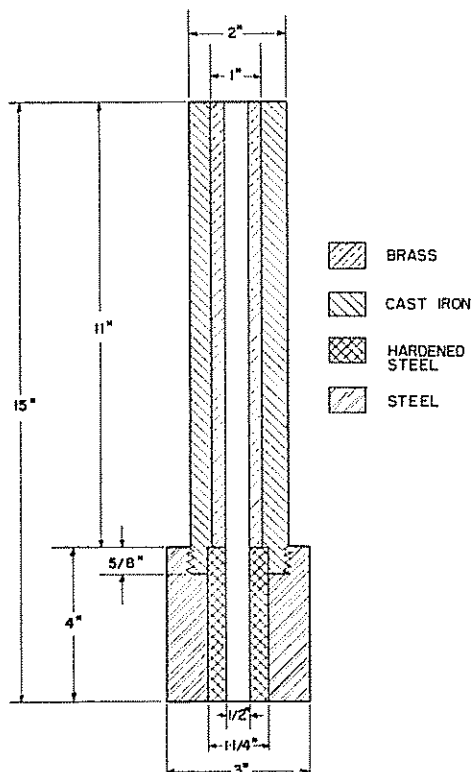


FIG. 1. Sketch of mold for compressing graphite.

bottom 4 in. section. About 1000 psi was required for this step, which could be accomplished easily by pushing the plunger in by hand. The top cast iron section was removed and the hardened steel plunger inserted in the bottom section. This assembly was put between the platens of a Baldwin Southwark Universal Testing Machine and pressure slowly applied until the final desired pressure was reached. The pressure was then released and the sample pushed from the mold. The samples were machined to exactly 1 in. in length using a lathe.

2. *Heat treating apparatus.* Heat treating of the molded samples was done in either a resistance or an induction furnace with a helium atmosphere maintained throughout the heating and cooling cycle.

3. *Reaction rate apparatus.* The apparatus and procedure used to determine the reactivity of the molded graphite specimens to carbon dioxide, flowing past the sample at one atmosphere pressure, have been described<sup>2,3</sup>.

4. *Gas adsorption apparatus.* A standard apparatus<sup>4</sup> was employed to determine adsorption isotherms for nitrogen at 77°K on the powdered and molded graphite samples. From the isotherms, specific surface areas were calculated using the BET equation<sup>4</sup>.

5. *Mercury porosimeter apparatus.* A mercury porosimeter was used to obtain macropore volume distributions in the molded graphite samples. A description of the design and operation of the porosimeter has been given<sup>5</sup>.

6. *Electrical resistivity apparatus.* Apparatus used for determining the electrical resistivity of the molded samples has been previously described<sup>6</sup>.

7. *X-ray diffraction apparatus.* A 164°(2θ) General Electric X-ray diffraction unit, XRD-3, with copper radiation, was used to determine interlayer spacings of the original and heat treated graphites. Also an indication of the extent of particle orientation in the molded samples was obtained from relative intensities of the (002) and (100) diffraction peaks. Graphite "slugs" 1/2 in. in diameter and 1/8 in. in thickness were cut from molded rods and mounted in an aluminum sample holder for the orientation work.

<sup>2</sup> P. L. Walker, Jr., R. J. Foresti, Jr. and C. C. Wright, *Industr. Engng. Chem.* **45**, 1703 (1953).

<sup>3</sup> P. L. Walker, Jr. and Emile Rauts, *J. Phys. Chem.* **60**, 364 (1956).

<sup>4</sup> P. H. Emmett, *A.S.T.M. Tech. Publ.* **51**, 95 (1941).

<sup>5</sup> P. L. Walker, Jr., F. Rusinko, Jr. and E. Rauts, *J. Phys. Chem.* **59**, 245 (1955).

<sup>6</sup> P. L. Walker, Jr. and F. Rusinko, Jr., *Fuel*, **36**, 43 (1957).

Standard X-ray procedures were employed, as previously discussed in detail<sup>7</sup>.

8. *Crushing strength apparatus.* Crushing strengths were determined on the molded samples using a Baldwin Southwark Universal Testing machine. For all samples tested, the first noticeable sign of fracture was a spalling-off of some graphite near the ends of the sample (next to the platens of the machine). In some cases, cracks next began to develop through the sample. Finally, the sample would fracture completely; this pressure was taken as the fracture pressure.

### III. RESULTS AND DISCUSSION

#### A. Selected Properties of the Original and Heat Treated Graphite Flours

1. *Spectrochemical analyses.* Table I presents data on the ash analyses of the original graphite and a sample soaked at 2600°C for

TABLE I  
Spectrochemical Ash Analyses of Graphites  
(Per Cent)

Elements Detected	Original	Heat Treated
Si	0.5	0.004
Fe	0.2	0.002
Al	0.004	0.001
Mg	0.004	0.000 <sub>x</sub>
Ti	0.000 <sub>x</sub>	ND
Cu	0.04	0.000 <sub>x</sub>
Mn	0.004	ND
Cu	0.014	0.010
Pb	<0.005	ND
Nu	0.0004	0.000 <sub>x</sub>
K	0.05	0.001

ND = Not Detected

Elements sought but not detected: Ag, As, Au, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Ga, Ge, Hg, La, Li, Mo, Nb, Ni, P, Rb, Sb, Sn, Sr, V, Zn, and Zr.

30 min. As expected, there was a substantial decrease in impurity content in the graphite following heat treatment at this elevated temperature.

2. *Crystallographic structure.* The interlayer spacing of the original graphite and a sample

soaked at 2600°C for 30 min was  $3.3543 \pm 0.0001$  Å at 15°C. This value is in close agreement with that reported by Nelson and Riley<sup>8</sup> for Ceylon natural graphite—3.3538 Å at 15°C. The crystallite sizes of the original and heat treated samples, as estimated from X-ray diffraction line broadening (using sodium chloride as an internal standard), were above 1000 Å.

3. *Surface area.* The surface area of the original graphite was 11.6 m<sup>2</sup>/g. Upon heat treatment to 2400 and 2800°C, the area decreased to 9.2 and 8.5 m<sup>2</sup>/g, respectively. The decrease in area upon heat treatment can be attributed to a decrease in particle porosity and surface roughness paralleling an increase in crystallite orientation. The relatively small decrease in area is indicative of a high degree of crystallite orientation in the original material.

#### B. Selected Properties of Molded, Original Graphite

1. *Apparent density.* Samples were molded using initial sample weights of 6, 7, and 8 g to final molding pressures of 11,500, 31,500, and 125,000 psi, respectively. Under these conditions, samples having apparent densities of 1.61, 1.83, and 1.99 g/cm<sup>3</sup> were produced. The apparent densities could be duplicated within  $\pm 0.2\%$ .

Variation in the radial density of the molded samples was investigated briefly, by comparing densities before and after a  $\frac{1}{8}$  in. hole was drilled down the axis of the rods. Excellent uniformity was found, with the densities in no instance varying by more than 1%.

Variation in the longitudinal density was investigated by cutting successive segments from the sample. A gradual decrease in density of sample was observed with increase in distance from the plunger. Over a 1 in. sample length, the incremental density varied by ca. 10%. This density variation doubtless

<sup>7</sup> P. L. Walker, Jr., H. A. McKinstry and J. V. Pustinger, *Industr. Engng. Chem.* **46**, 1651 (1954).

<sup>8</sup> J. B. Nelson and D. P. Riley, *Proc. Phys. Soc.* **57**, 477 (1945).

could have been improved somewhat by using a double-acting plunger.

Within reasonable limits, a negligible effect of rate of pressure application and holding-time at the final pressure on the apparent density was found.

2. *Hardness.* Scleroscope hardness was determined on the molded samples in a direction perpendicular to the axis of the rods.

4. *Orientation of particles.* It is known that Ceylon natural graphite particles are flake-like, with the carbon basal planes in the crystallites highly oriented parallel to the long side of the particles<sup>7</sup>. It was expected, therefore, that on molding, the particles would be oriented strongly with their long side (basal planes) perpendicular to the molding direction. An attempt was made to follow

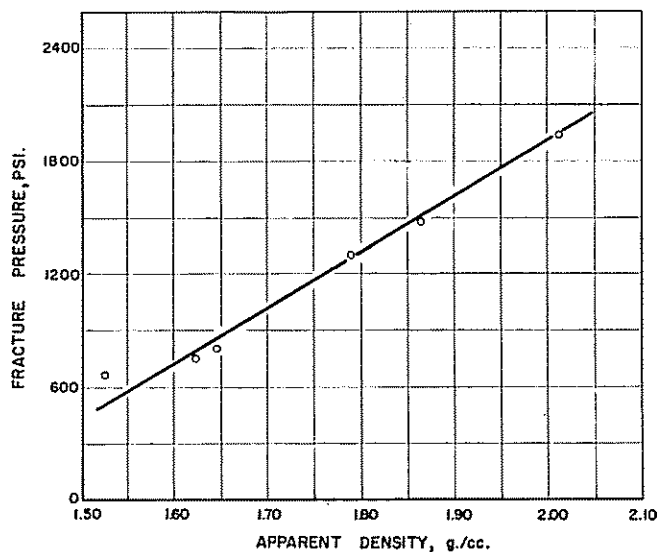


FIG. 2. Crushing strengths of graphites molded at various densities.

Negligible variation could be found with change in molding pressure, the values ranging from 8.5 to 9.3. These values can be compared with those for typical baked and graphitized carbon bodies of 80 and 30, respectively.

3. *Crushing strength.* Figure 2 shows the variation of crushing strength with apparent density of the molded samples. A marked effect is noted. For comparison, typical graphitized carbon bodies have crushing strengths increasing from ca 3,000 to 5,000 psi as their apparent densities<sup>9</sup> increase from 1.5 to 1.7 g/cm<sup>3</sup>.

<sup>9</sup> H. W. Abbott, *Encyclopedia of Chemical Technology*, Vol. 3, The Interscience Encyclopedia, Inc., New York, N.Y., 1949, p. 29.

the variation in orientation with molding pressure by determining the ratio of intensities of the (002) to (100) X-ray diffraction peaks, as discussed in the experimental section. The attempt was unsuccessful, however, since even at the lowest molding pressure no (100) diffraction peak could be distinguished above the background. On the other hand, the (002) diffraction peak was extremely strong, at all molding pressures, producing a ratio of peak intensities in excess of 1500. Since the theoretical ratio of intensities for the (002) and (100) diffraction peaks (absence of orientation) is about 40<sup>10</sup>, a high degree of orientation in the molded rods is clearly evident.

<sup>10</sup> Private communication from H. A. McKinstrey.

5. *Surface area.* The surface area of the sample molded to a density of  $1.99 \text{ g/cm}^3$  was  $11.3 \text{ m}^2/\text{g}$ , a negligible decrease from the area of the graphite flour. This is taken as evidence that the molding operation had not blocked off an appreciable area accessible to nitrogen at  $77^\circ\text{K}$ .

It should be noted that up to four days was required to outgas the molded samples at  $225^\circ\text{C}$  to a pressure of less than  $0.1 \mu$ . The time required for outgassing increased with increase in density of the sample. From these results, it is concluded that the rate of transport of gas through the pore system of the molded samples was slow. On the other hand, for the adsorption runs at  $77^\circ\text{K}$ , equilibration of each isotherm point was reached in several minutes. Apparently rapid, two-dimensional surface migration of condensed nitrogen was taking place<sup>11,12</sup>.

6. *Effect of heat treatment on dimensional changes of molded rods.* Heat treatment produced some noticeable changes in the molded samples. From weight determinations on 25 samples before and after heat treating to  $2600^\circ\text{C}$ , an average weight loss of  $3.44\%$  was found. This value is compared to the ash content of the original Ceylon graphite of  $2.05\%$ . The difference in these figures probably can be accounted for primarily by sublimation of carbon, since the volatile matter content of the original graphite was quite low.

An expansion of the samples occurred during the heat treatment, probably caused by the escape of impurities. Table II summarizes the results for three molding pressures. It is of interest to note that the percentage increase in diameter was greater the higher the molding pressure; whereas, the percentage increase in length was smaller the higher the molding pressure. As a result, the percentage decrease in density of the

TABLE II  
*Changes in Physical Dimensions of Molded Rods Induced by Heat Treatment at  $2600^\circ\text{C}$*

Molding Pressure, psi	Diameter Increase, per cent	Length Increase, per cent	Density Decrease, per cent
11,500	1.25	6.83	12.28
31,500	1.48	5.50	11.15
125,000	1.86	4.26	11.66

samples upon heat treatment was relatively independent of molding pressure. Samples heated at temperatures below  $2600^\circ\text{C}$  were found to undergo intermediate amounts of expansion.

### C. Reactivity of Molded Graphite to Carbon Dioxide

1. *Effect of heat treatment temperature and soak time.* Reaction rate curves were typical in shape to those previously found in studies of the carbon-carbon dioxide reaction<sup>2,13</sup>. That is, there was an initial, gradual increase in reaction rate up to *ca.* 2 per cent burn-off, followed by an extended burn-off region at constant reaction rate. The reactivity results were taken from the constant-rate portion of each run.

Samples compacted at 31,500 psi were heat treated at a series of temperatures between  $1556$  and  $3017^\circ\text{C}$  for varying soak times. Their subsequent reactivities to carbon dioxide at  $1000^\circ\text{C}$  are reported in Table III. Also listed in Table III are the average and maximum temperatures over the soak period. Sample 2600R, on which more detailed reactivity results will be presented, was treated in a resistance furnace; the remainder of the samples were heated in an induction furnace. It is seen from Table III that heat treatment produced a marked decrease in the reactivity of compacted Ceylon natural graphite. In the most extreme case, heat treatment at an average temperature of  $3017^\circ\text{C}$  for 20 min resulted in a 27-fold decrease in reactivity.

<sup>11</sup> R. H. Tomlinson and E. A. Flood, *Canad. J. Res.*, B26, 38 (1948).

<sup>12</sup> Ahlborn Wheeler, *Advances in Catalysis*, Vol. III, Academic Press, New York, N.Y., 1951, p. 273.

<sup>13</sup> P. L. Walker, Jr. and F. Rusinko, Jr., *J. Phys. Chem.*, 59, 241 (1955).

TABLE III  
*Effect of Heat-treatment Temperature and Soak Time on Reactivity of Compressed Ceylon Natural Graphite to Carbon Dioxide at 1000°C*

Heat-treatment Temperature, °C		Soak Time Hours	Reaction Rate Grams per Hour
Average	Maximum		
Original	—	—	1.316
1556	1590	1	0.382
1615	1690	4	0.314
2002	2008	1	0.334
2025	2040	4	0.157
2600R	—	½	0.103
2599	2610	1	0.055
2580	2615	4	0.052
3017	3030	½	0.048

The results further suggest that an increase in soak time at a particular temperature can also decrease reactivity, even though difficulties in maintaining the maximum temperature a constant for different soak times makes this effect somewhat difficult to evaluate. Nevertheless, results showing that a soak time of 4 hr at 1615°C produced a lower reactivity than a soak time of 1 hr at 2002°C strongly support the importance of soak time.

Probably the decrease in reactivity of compacted Ceylon natural graphite with an increase in severity of heat treatment (higher temperatures and longer soak times) is related to a decrease in concentration of impurities, which catalyze the gasification reaction. Spectrochemical analyses were determined on all the heat treated samples. In general, the purity of the sample increased with increasing heat treatment temperature and increasing soak time at a particular temperature. However, no correlation could be found between the change in concentration of particular elements and the subsequent reactivity of the carbon. The conclusion that the removal of impurities from the graphite was responsible for the reactivity-decrease is further substantiated by the effect of heat treatment on other properties of the molded samples. Heat treatment was found to decrease the apparent density of the molded

samples, which in turn should have increased the rate of gas diffusion through the samples. An increase in rate of gas diffusion could only increase reactivities. Heat treatment was found to decrease the surface area of the graphite only slightly and to produce no detectable changes in crystallite size or orientation.

2. *Effect of reaction temperature and apparent density of molded graphite.* Molded samples of the original graphite and material heated to 2600°C were reacted to 10% burn-off at 900, 1000, and 1100°C. In addition, molded samples of the original graphite were reacted at 800°C. Results are presented in Table IV.

TABLE IV  
*Reaction Rates of Graphites at Various Temperatures*

Molding Pressure, psi	Apparent Density, g/cm <sup>3</sup>	Reaction Temperature, °C			
		800	900	1000	1100
		Reaction Rate of Original Graphite, g/hr			
11,500	1.61	0.037	0.187	1.407	3.190
31,500	1.83	0.033	0.190	1.316	3.200
125,000	1.99	0.032	0.240	1.290	3.360
		Reaction Rate of Heat-treated Graphite, g/hr			
11,500	1.41	—	0.018	0.097	0.487
31,500	1.63	—	0.014	0.103	0.470
125,000	1.76	—	0.015	0.090	0.442

Surface area and apparent density determinations were made on all the samples gasified to 10% burn-off at the various temperatures. The data are presented in Tables V and VI. It is seen from the data that the surface area of the Ceylon graphite was not greatly increased upon reaction with carbon dioxide. The area which was developed, however, is a function of both the starting apparent density of the molded sample and the reaction temperature. As expected, apparent densities of the molded samples decreased upon reaction. For samples of the original graphite molded to the

TABLE V

*Surface Area, Density, and Porosity of Original Graphite Gasified at Various Temperatures*

Reaction Temperature, °C	Total Area, m <sup>2</sup>	Specific Area, m <sup>2</sup> /g	Apparent Density, g/cm <sup>3</sup>	Pore Volume, cm <sup>3</sup> /g
Molding Pressure, 11,500 psi				
Unreacted	56.8	11.6	1.590	0.1882
800	63.8	14.4	1.372	0.2882
900	59.9	13.7	1.363	0.2930
1000	93.1	21.3	1.375	0.2866
1100	96.3	22.1	1.368	0.2903
Molding Pressure, 31,500 psi				
Unreacted	64.5	11.6	1.815	0.1104
800	68.3	13.7	1.567	0.1975
900	72.1	14.5	1.578	0.1930
1000	96.1	19.5	1.544	0.2070
1100	90.3	18.5	1.540	0.2086
Molding Pressure, 125,000 psi				
Unreacted	70.6	11.6	1.923	0.0793
800	76.0	13.9	1.705	1.1458
900	91.2	16.7	1.721	0.1403
1000	96.3	17.7	1.701	0.1472
1100	90.7	16.8	1.695	0.1493

TABLE VI

*Surface Area, Density, and Porosity of Heat Treated Graphite Gasified at Various Temperatures*

Reaction Temperature, °C	Total Area, m <sup>2</sup>	Specific Area, m <sup>2</sup> /g	Apparent Density, g/cm <sup>3</sup>	Pore Volume, cm <sup>3</sup> /g
Molding Pressure, 11,500 psi				
Unreacted	38.5	8.7	1.396	0.2756
900	54.4	13.7	1.341	0.3050
1000	58.5	14.8	1.319	0.3174
1100	94.5	23.7	1.309	0.3232
Molding Pressure, 31,500 psi				
Unreacted	44.6	8.7	1.614	0.1789
900	56.4	12.3	1.572	0.1954
1000	70.9	15.4	1.530	0.2129
1100	101.5	22.1	1.488	0.2313
Molding Pressure, 125,000 psi				
Unreacted	49.0	8.7	1.756	0.1294
900	66.9	13.2	1.695	0.1493
1000	82.0	16.2	1.648	0.1661
1100	112.9	22.4	1.611	0.1880

same apparent density, reaction at various temperatures produced a decrease in apparent density which was essentially independent of reaction temperature. In contrast to this, apparent densities of the heat treated samples decreased progressively as reaction temperature was increased.

From knowledge of the total surface area of the molded samples at 10% burn-off, it is possible to calculate the specific reactivity of the samples. These data are presented in Table VII. The pressure of carbon dioxide

TABLE VII

*Specific Reactivities of Graphites*

Reaction Temperature, °C	Apparent Density, g/cm <sup>3</sup>	Specific Reactivity g/hr per atmosphere CO <sub>2</sub> /m <sup>2</sup>
Original Graphite		
800	1.61	0.00058
800	1.83	0.00048
800	1.99	0.00042
900	1.61	0.00314
900	1.83	0.00265
900	1.99	0.00264
1000	1.61	0.01544
1000	1.83	0.01400
1000	1.99	0.01368
1100	1.61	0.03484
1100	1.83	0.03728
1100	1.99	0.03905
Heat-treated Graphite		
900	1.41	0.00033
900	1.63	0.00025
900	1.76	0.00022
1000	1.41	0.00166
1000	1.63	0.00145
1000	1.76	0.00110
1100	1.41	0.00520
1100	1.63	0.00466
1100	1.76	0.00394

was taken as the average pressure at the outside of the rod and was calculated from the amount of carbon dioxide entering the reactor and the amount of carbon reacting per unit time. Figure 3 summarizes the specific

reactivity data using an Arrhenius plot. To a close approximation, the reactivities for the original and heat treated samples were  $1.5 \times 10^5 e^{-42,000/RT}$  and  $1.7 \times 10^4 e^{-42,000/RT}$ , respectively. Thus, heat treatment (and purification) of the Ceylon natural graphite at

Zone II<sup>16</sup>. Zone II is the intermediate temperature zone in a heterogeneous reaction where the concentration of the reactant species goes to zero (or its equilibrium value) at a distance from the exterior surface less than the radius of the rod. The reaction rate

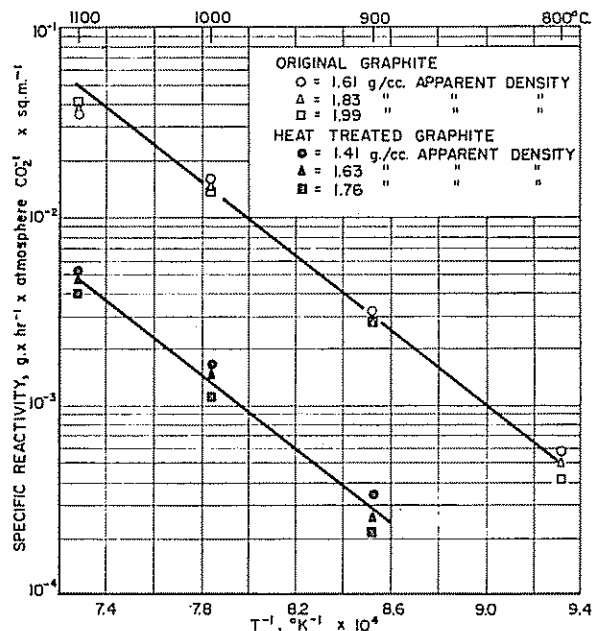


Fig. 3. Arrhenius plots of specific reactivity of graphite with carbon dioxide.

2600°C is seen to have decreased by a factor of about 10 the fraction of the total surface area participating in the reaction but not to have affected the activation energy of the reaction.

It is noted that the activation energy for the carbon-carbon dioxide reaction found in this work ( $42 \pm 2$  kcal/mole) is very close to one-half of 86 kcal/mole, which is recommended as the true activation energy for this reaction by Wicke<sup>14</sup> and Rossberg<sup>15</sup>. A value of one-half the true activation energy would be expected if the reaction was proceeding in

is controlled jointly by the rate of mass transport of the reactant through the interior of the sample and the inherent chemical reactivity of the carbon.

Other experimental results substantiate the belief that the present reactivity runs were conducted in Zone II. As previously reported, the time required to degas the molded samples preparatory to adsorption runs was excessively long. This indicates that the mass transport rate of gas through the rods was low and would be expected to be one factor controlling the reaction rates. Further, in

<sup>14</sup> E. Wicke, *Fifth Symposium on Combustion*, Reinhold Publishing Corp., New York, 1955, p. 245.

<sup>15</sup> M. Rossberg, *Z. f. Elect.* **60**, 952 (1956).

<sup>16</sup> P. L. Walker, Jr., Frank Rusinko, Jr. and L. G. Austin, Gas Reactions of Carbon, *Advances in Catalysis*, Vol. XI, Academic Press, New York, 1959, p.133.



Zone II, for a carbon having a fixed inherent chemical reactivity, its specific reactivity should increase as the diffusion rate of the reacting gas into the sample increases. Since the diffusion rate of a gas into a porous carbon is known to increase as the apparent density

samples. Little pore volume is seen to exist at pore radii above 1000 Å in any of the samples. For the lower density samples, large amounts of pore volume appear in the radius range 400 to 800 Å. Thus, the macropore size at which there was a large accumulation of

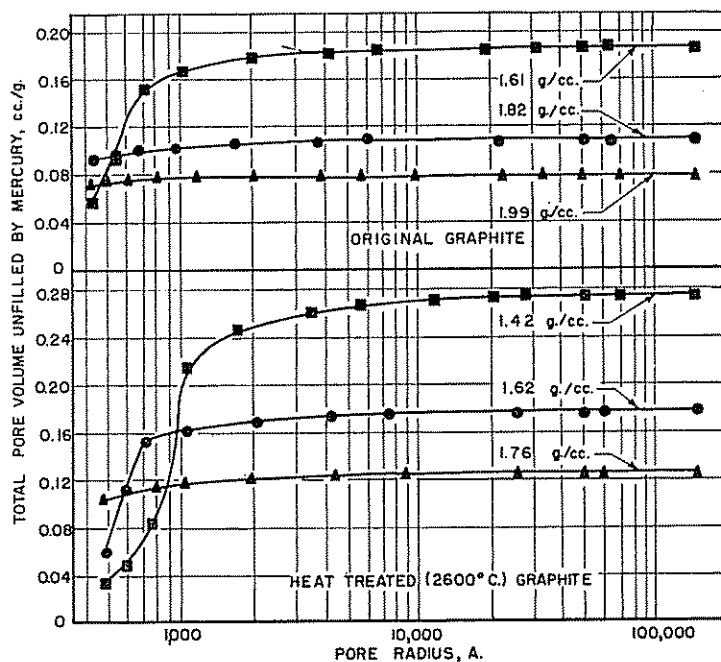


FIG. 4. Macropore volume distribution in original and heat treated (2600°C) molded graphite rods.

of the carbon decreases<sup>16</sup>, it is in turn expected that the specific reactivity in Zone II will increase with a decrease in apparent density of the sample. This is clearly seen to be the case for all of the reactivity data for the heat treated graphite. For the original graphite, the apparent density is seen to have a similar effect on reaction rates up to 1100°C. The reactivity data at 1100°C are not expected to show the same relation between rate and apparent density, since the reaction appears to be in the transition region between Zones II and III<sup>16</sup>.

3. *Volume distribution of macropores in molded rods.* Figure 4 presents macropore volume distribution curves for the original and 2600°C heat treated molded graphite

pore volume was not only a function of the particle size distribution of the material making up the body, as previously discussed<sup>5</sup>, but also was a function of the extent of compaction of the particles. Unfortunately, the mercury porosimeter was not capable of going to pressures sufficiently high to locate the position of any large accumulation of pore volume in the higher density samples.

Insight into how the samples were reacting with carbon dioxide is obtained from macropore volume distribution curves on rods gasified to 10% burn-off. Figure 5 presents data for the molded, original graphite having an initial density of 1.61 g/cm<sup>3</sup>. It is seen that the new porosity developed on gasification is primarily in the pore size range above

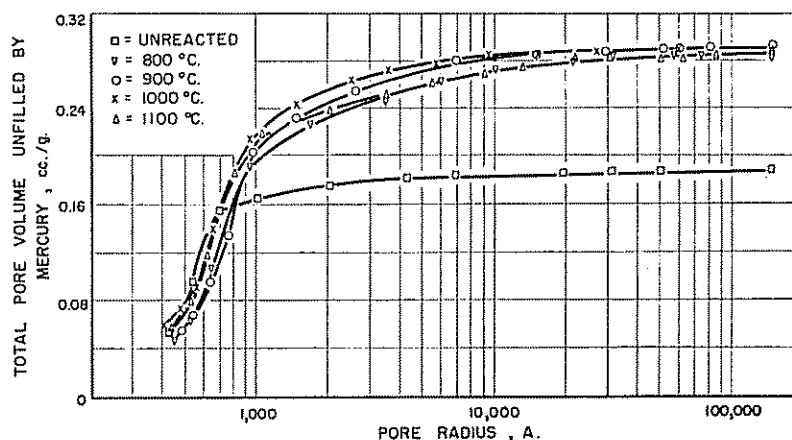


FIG. 5. Change in macropore volume of original graphite (apparent density = 1.61 g/cm<sup>3</sup>) at various reaction temperatures.

750 Å—the pore size at which a large macroporosity appears in the original rod. This fact suggests that reaction was primarily occurring by reduction in particle size of the graphite with an attendant increase in pore volume and pore size between particles. This conclusion is consistent with the surface area results which showed relatively minor increases in area with burn-off. As Smith and Polley<sup>17</sup> have shown, when oxidation of carbon primarily occurs at the surface of the particle, surface area increase is small. On the other hand, oxidation through the particle, with a negligible decrease in particle size, results in large increases in area<sup>17</sup>. The fact that the reaction of the natural graphite particles occurred primarily at their surface is consistent with the homogeneous nature of the surface<sup>17,18</sup>.

Macropore volume distributions of the other samples after gasification lead to similar conclusions.

4. *Electrical resistivities of molded graphite samples before and after gasification.* Electrical resistivity measurements were made on samples of the original and heat treated molded graphites. As seen in Fig. 6, the

electrical resistivity of both the original and heat treated samples decreased essentially linearly with increase in apparent density. However, the heat treated material is seen to have an appreciably lower resistivity than the original graphite at comparable densities. Possibly this is related to the amount of oxygen which the graphite has on its surface. That is, from water vapor adsorption<sup>19</sup>, it was estimated that 13.2% of the original graphite surface contained oxygen, whereas only 0.60% of the 2600°C heat-treated material contained an oxygen complex. The greater change in electrical resistivity with change in apparent density (molding pressure) for the molded original graphite is also consistent with its surface containing more oxygen complex.<sup>20</sup>

Typical carbon bodies containing a binder phase have considerably lower electrical resistivity values than those presented in Fig. 6, whether the samples are molded or extruded<sup>21</sup>. In particular, a sample of AGOT graphite (with a conventional petroleum coke base and pitch binder and density of 1.70

<sup>17</sup> W. R. Smith and M. H. Polley, *J. Phys. Chem.* **60**, 689 (1956).

<sup>18</sup> F. Rusínko, Jr. and P. L. Walker, Jr., "Anomalous Results for the Sorption of Argon on Powdered Natural Graphite", submitted for publication.

<sup>19</sup> F. H. Healey, Yung-Fang Yu, and J. J. Chessick, *J. Phys. Chem.* **59**, 399 (1955).

<sup>20</sup> S. Mrozowski, *Proc. Third Carbon Conf.* Pergamon Press (1959), p. 495.

<sup>21</sup> W. W. Tyler and A. C. Wilson, Jr., *Phys. Rev.* **89**, 870 (1953).

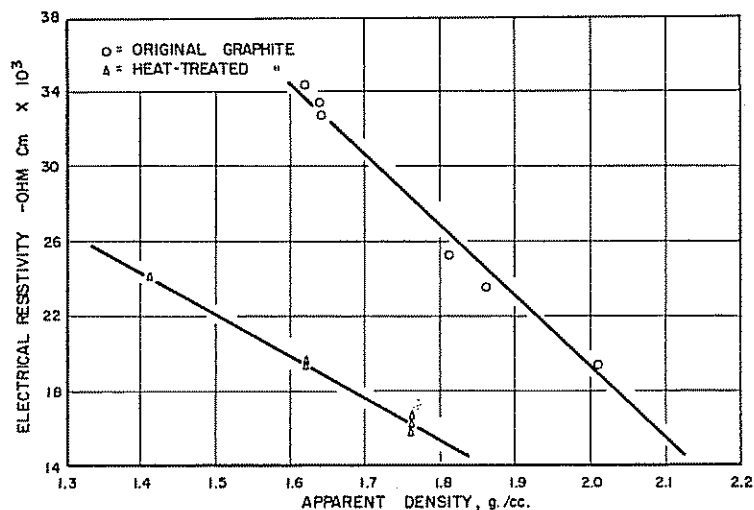


Fig. 6. Electrical resistivity of graphites at various apparent densities.

$\text{g/cm}^3$ ) has a room-temperature resistivity of  $1.1 \times 10^{-3} \Omega \text{ cm}$  in the direction perpendicular to preferential basal plane orientation.

#### IV. CONCLUSIONS

Ceylon natural graphite can be easily molded at room temperature into bodies of varying apparent densities depending upon the molding pressure. These molded samples have crushing strengths and electrical conductivities considerably lower than conven-

tional graphite bodies (containing a filler and binder phase) of comparable apparent densities. Reactivity of the original molded graphite to carbon dioxide can be reduced greatly by heat treating to temperatures where removal of metallic impurities is effected. The decrease in reactivity is brought about by decreasing the fraction of carbon surface active to carbon dioxide and not by lowering the activation energy of the reaction.

