

Reprinted from "Proceedings of 1957 Conference on Carbon"  
 PERGAMON PRESS  
 LONDON · NEW YORK · PARIS · LOS ANGELES  
 Printed in Great Britain by The Chapel River Press, Andover, Hants

EFFECT OF IMPREGNATION AND SUBSEQUENT BURN-OFF ON PHYSICAL  
 PROPERTIES OF GRAPHITIZED CARBON RODS\*

P. L. WALKER, JR. AND F. RUSINKO, JR.  
 Department of Fuel Technology  
 The Pennsylvania State University, University Park, Pennsylvania.

(Manuscript received November 5, 1957)

Graphitized carbon rods were impregnated three, seven, and twelve times with a low melting point pitch and the samples then baked at ca. 790°C. The original rods are shown to have a significant closed pore volume, which is appreciably opened up upon burn-off. Impregnation is found progressively to lower the specific surface area and macroporosity (porosity primarily between particles) in the rods. Subsequent gasification of the rods to "constant" burn-off at different temperatures is seen to change the surface areas, helium densities, apparent densities, and porosities of the rods in ways which are qualitatively explainable. The impregnated rods are found to have higher gasification rates than the original rods with carbon dioxide at 1000 and 1100°C, which is a result of the high reactivity of the impregnant. At 900°C, the higher surface area of the unimpregnated rods counterbalances the higher reactivity of the impregnant and results in essentially a constant rate for all rods. Changes in electrical resistivity of the rods, as a function of impregnation and subsequent burn-off, are presented. The diffusion rate of gas through the rods is seen to be markedly decreased by impregnation.

I. INTRODUCTION

Normally, the raw materials going into the manufacture of baked and graphitized carbon products consist of ca. 70% sized, sized petroleum coke flour and 30% coal tar pitch filler by weight. Upon baking, ca. 50% of the pitch is lost leaving a final product containing ca. 80% petroleum-coke-carbon and 20% coal-tar-pitch-carbon. These proportions remain essentially the same after graphitization.

The resulting body has a porosity of around 30%<sup>1</sup>, with the porosity primarily concentrated in interconnecting macropores greater than 1 $\mu$  in radius<sup>2</sup>. This macroporosity is created by the void volume between the petroleum coke particles.

With the possibility of using carbon shapes as heat exchanger tubes, absorption towers, pump parts, and moderators in liquid metal

reactors appreciated, the need for a less porous body was immediately apparent. Diffusion and forced flow in and through the porous network of ordinary carbon could not be tolerated.

At least three approaches have been used to decrease this porosity: (1) Incorporate in with the petroleum coke flour a thermostable carbon of small particle size to fill the voids between coke particles<sup>3</sup>. (2) Increase the coking value of the pitch by the addition of a nitro substituted organic compound<sup>4</sup>. (3) Fill the macropores of the baked or graphitized sample with additional pitch by impregnation<sup>5</sup>. While all of these processes have met with some success for particular applications, impregnation has been found to be the most satisfactory of these three techniques for attaining an impervious material.

\*This paper presents the results of one phase of research carried out under Contract No. AT(30-1)-1710, sponsored by the Atomic Energy Commission.

<sup>1</sup> P. L. Walker, Jr. and F. Rusinko, Jr. *J. Phys. Chem.* **59**, 241 (1955).

<sup>2</sup> P. L. Walker, Jr., F. Rusinko, Jr. and E. Raats, *J. Phys. Chem.* **59**, 245 (1955).

<sup>3</sup> Lloyd C. Swallen and Harold W. Nelson, *U.S. Pat.* 2,527,595 October 31 (1950).

<sup>4</sup> Frederick L. Shea, Jr. and Leslie H. Juel, *U.S. Pat.* 2,527,596, October 31 (1950).

<sup>5</sup> H. W. Abbott, *Encyclopedia of Chemical Technology*, Vol. 3, p. 17, Interscience Encyclopedia Inc., New York (1949).

In this paper the effect of varying degrees of impregnation followed by subsequent burn-off on the physical properties of graphitized carbon rods has been investigated.

## II. EXPERIMENTAL

### A. Carbon

The unimpregnated samples were National Carbon Company's AGHT graphitized rods 8 in. long and  $\frac{9}{16}$  in. in diameter. Different batches of these rods were impregnated three, seven and twelve times with a low melting point pitch. After impregnation, the rods were baked at 790°C to coke the pitch. Results to be presented later also suggest that somewhere between seven and twelve impregnations the rods were unexpectedly slightly oxidized.

### B. Low Temperature Gas Adsorption Apparatus

A standard gas adsorption apparatus was employed and has been described recently<sup>6</sup>. Because of the low surface areas encountered for the impregnated rods, krypton adsorption at liquid nitrogen temperature was used, as discussed by Beebe *et al.*<sup>7</sup>. Nitrogen adsorption was used on the unimpregnated and reacted samples. Surface areas were calculated using the *BET* equation<sup>8</sup>.

### C. Mercury Porosimeter

A description of the design and operation of the mercury porosimeter used has been given recently<sup>2</sup>. The porosimeter was used to determine the volume-distribution of macropores in the samples over the radius range 410–140,000 Å and also the apparent density of the samples by mercury displacement under an absolute pressure of ca. 360 mm Hg.

### D. Electrical Resistivity Apparatus

Essentially the electrical resistivity of the

cylindrical specimens was determined by comparing the voltage drop across a known sample length with that across a fixed resistance both carrying the same total current. Further details of the technique are discussed elsewhere<sup>9</sup>.

### E. X-ray Diffraction Apparatus

A 164° (2θ) General Electric X-ray diffraction unit, XRD-3, with copper radiation was used to determine spacings for the carbon samples. Spacing values of high accuracy were determined using NaCl as an internal standard as previously discussed<sup>10</sup>. The interlayer spacing and carbon-carbon spacing in the layer plane were used to calculate the X-ray density of the carbon in the standard manner.

### F. Gas Diffusion Apparatus

The effective diffusion coefficients for hydrogen-nitrogen through  $\frac{1}{8}$  in. long by  $\frac{1}{8}$  in. diameter carbon samples cut from the larger rods were determined by techniques previously discussed<sup>1</sup>.

### G. Reaction Rate Apparatus

The reactor was the same as that used in previous gasification studies<sup>6</sup>. Samples 2 in. long by  $\frac{9}{16}$  in. in diameter were reacted with carbon dioxide at atmospheric pressure at temperatures ranging from 900 to 1100°C. The samples were suspended in the reactor by a ceramic support, as described recently<sup>11</sup>.

### H. 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  $30.0 \pm 0.1^\circ\text{C}$ ) was of the constant pressure type; that is, after the expansion

<sup>6</sup> P. L. Walker, Jr., R. J. Foresti, Jr. and C. C. Wright, *Ind. Eng. Chem.* **45**, 1703 (1953).

<sup>7</sup> Ralph A. Beebe, John B. Beckwith and Jurgen M. Honig, *J. Amer. Chem. Soc.* **67**, 1554 (1945).

<sup>8</sup> P. H. Emmett, *A.S.T.M. Tech. Publ.* **51**, 95 (1941).

<sup>9</sup> P. L. Walker, Jr. and Frank Rusinko, Jr., *Fuel*, **36**, 43 (1957).

<sup>10</sup> P. L. Walker, Jr., H. A. McKinstry and J. V. Pustinger, *Ind. Eng. Chem.* **46**, 1651 (1954).

<sup>11</sup> P. L. Walker, Jr. and Emile Raats, *J. Phys. Chem.* **60**, 364 (1956).

of the helium into the sample bulb, the pressure was returned 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 1 hr was allowed after exposing the sample to the helium gas. Helium densities could be duplicated to within  $\pm 0.5\%$ .

### III. RESULTS AND DISCUSSION

#### A. Pore Volume and Surface Area of Rods as Affected by Impregnation and Subsequent Burn-Off

The total pore volume within graphitized carbon rods may be arbitrarily defined as consisting of two types—that which is open to helium penetration and that which is closed. The total pore volume, expressed in ml/g, is calculated from the difference of the reciprocals of apparent and X-ray densities. The open pore volume, expressed in ml/g, is calculated from the difference of the reciprocals of apparent and helium densities. The closed pore volume is the difference between the total and open pore volumes. Dresel and Roberts<sup>12</sup> investigated an unimpregnated graphitized carbon and showed that it contained some closed pore volume and that this volume was appreciably opened up by oxidizing the sample in air at 430–500°C to small burn-offs. Loch and Austin<sup>13</sup> showed that the magnitude of the closed pore volume in a number of graphitized carbon bodies, which they investigated, could be related to the carbon crystallite size, the smaller the crystallite size the higher the percentage of the closed pore volume.

Table I presents data on the closed pore volume in the unimpregnated rods used in

<sup>12</sup> E. M. Dresel and L. E. J. Roberts, *Nature, Lond.* **171**, 170 (1953).

<sup>13</sup> L. D. Loch and A. E. Austin, *Proc. 1st and 2nd Carbon Conf.*, University of Buffalo (1956) pp. 65–73.

TABLE I

*Effect of 11% Burn-Off at Varying Gasification Temperatures on Decreasing Closed Pore Volume in Unimpregnated Rods*

Burn-off temp., °C	Closed pore vol. in total pore vol. %	Closed pore vol. in total sample vol. %
Unreacted	20.0	5.6
900	9.5	3.3
1000	8.4	2.9
1100	6.7	2.3

this work and its change upon 11% burn-off at different temperatures. These values were calculated from helium and apparent density data, to be discussed shortly, and from an X-ray density of 2.263 g/ml, based on an interlayer spacing value of 3.3592 Å (15°C) and a C–C bond distance in the layer plane of 1.416 Å. There is substantial agreement between the percentage closed pore volume found by Dresel and Roberts and by the authors, but Dresel and Roberts did observe a much more marked decrease in closed pore volume, at even smaller burn-offs than did the authors. Undoubtedly the success of opening up closed pore volume is a function of the physical structure of the starting material, the reactant gas (i.e. air, carbon dioxide, steam or hydrogen), and the reaction temperature. In the present work, as observed in Table I, the closed pore volume is opened up to the greatest extent at the highest reaction temperature.

Table II presents data on the change in physical properties of graphitized carbon rods on impregnation\*. As would be expected, the specific surface area of the rods decreases with increasing impregnation. However, since the specific, geometric surface area for rod<sub>1,2</sub> is 0.002 m<sup>2</sup>/g and the BET area is 0.09 m<sup>2</sup>/g (surface roughness factor of 45), it is seen that even with twelve impregnations considerable internal porosity is still connected to the surface.

\*In the future discussion, for simplicity, the number of impregnations given a rod will be frequently indicated by rod<sub>0</sub>, rod<sub>3</sub>, rod<sub>7</sub>, and rod<sub>12</sub>.

TABLE II

*Changes in Physical Properties of Graphitized Carbon Rods on Impregnation*

Number of impregnations	Weight % of impregnant in sample	Surface area m <sup>2</sup> /g	Helium density g/ml	Apparent density g/ml	Total open porosity %	Percentage macroporosity in total open porosity*
0	0.0	0.31	2.110	1.641	22.2	91.5
3	6.6	0.18	2.030	1.746	14.0	89.2
7	9.2	0.13	1.962	1.821	7.2	98.1
12	11.7	0.09	2.033	1.865	8.3	67.8

\* This includes pores greater than 420 Å in radius, as determined from the mercury porosimeter data.

From Table II, it is seen that through seven impregnations, the helium density decreases, as would be expected. Since the impregnant is only heated to 790°C, it is still amorphous and, consequently, has a lower density than the graphitized carbon-skeleton. However, after twelve impregnations, the helium density, in duplicate runs, surprisingly increases above that of rod<sub>7</sub>. Since after each impregnation the rods were heated to 790°C to coke the pitch, the most reasonable explanation seems to be that somewhere between seven and twelve impregnations the rods were slightly oxidized, which resulted in the opening up of some closed pore volume. The opening up of some closed pore volume need not necessarily show up as an increase in surface area, however, since it is possible that at the low temperature at which krypton adsorption was conducted (77°K) activated diffusion prevented the adsorbate from reaching this area<sup>14</sup>.

On impregnation, the apparent density of the rods is seen to increase. The total open pore volume (porosity) decreases up to seven impregnations and then increases slightly with twelve impregnations, which is again suggestive of a slight oxidation.

The percentage macroporosity in the total open porosity is seen to be affected by impregnation. This macroporosity is determined from the mercury porosimeter curves

<sup>14</sup> P. L. Walker, Jr. and Irwin Geller, *Nature, Lond.* 178, 1001 (1956).

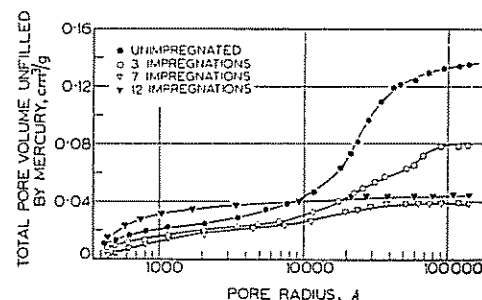


Fig. 1. Change in open macropore volume-distribution in graphitized carbon rods with varying degrees of impregnation.

of the rods, which are shown in Fig. 1\*. With three impregnations, there is a marked decrease in the magnitude of the macroporosity and only a slight decrease in microporosity, but the percentage decrease in the two porosities is essentially the same. Impregnation seven times again produces a significant reduction in macroporosity and practically eliminates open microporosity. It was suspected that the virtual elimination of microporosity was caused primarily by blocking as opposed to filling with impregnant. To check this hypothesis, the density of the impregnant in rod<sub>3</sub> and rod<sub>7</sub> was calculated from the weight of impregnant in the rod and the decrease in total open pore

\* The macropore distribution for the unimpregnated sample is very similar to that found previously by the authors<sup>2</sup> for a number of commercial carbons and graphites. The large amount of volume in pores between 1 and 5μ is produced primarily by voids between particles.

volume. The densities calculated for the coked impregnant are 1.66 and 1.22 g/ml, respectively. The lower, calculated density for the impregnant in rod<sub>7</sub> is qualitatively in agreement with the possibility that the impregnant did block off some micropore volume. In fact, if it is assumed that the difference in micropore volume in rod<sub>3</sub> and rod<sub>7</sub> (0.0078 ml/g), as given in Fig. 1, is all caused by pore blockage, the density of impregnant in rod<sub>7</sub> is still only increased to 1.35 g/ml. This suggests that with the seven impregnations some macroporosity, in addition to most, if not all, of the microporosity was blocked off. With twelve impregnations, the percentage of macroporosity is seen to decrease sharply in line with the possibility that slight oxidation opened up some of the closed micropores blocked after seven impregnations.

Figure 2 presents macropore volume-distribution plots showing the radial uniformity of impregnation, by looking at rods of varying diameter. For rod<sub>0</sub>, rod<sub>3</sub> and rod<sub>7</sub>, the macropore volume-distributions indicate a

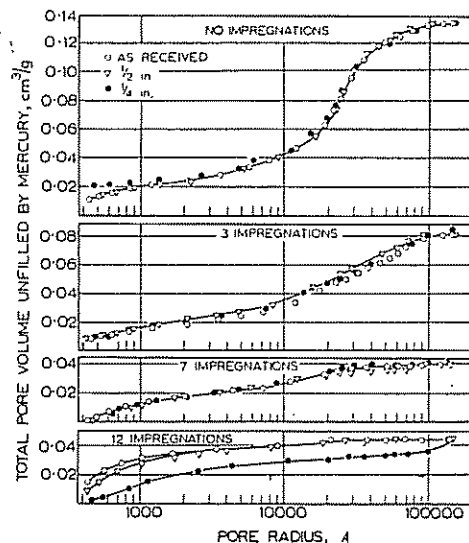


FIG. 2. Radial uniformity of impregnation through rods as shown by variation of macropore volume-distribution with sample diameter.

high degree of uniformity of impregnation through the rods. Again rod<sub>12</sub> shows anomalous results, which can be explained by assuming slight oxidation of the sample. First, the pore volume distribution below 10,000 Å in the 1/4 in. diameter sample is quite similar to that in rod<sub>7</sub> and suggests that the oxidation did not penetrate sufficiently deeply to open up closed pores at this depth. Further, as the sample diameter increases, it is seen that the amount of micropore volume which was opened up by oxidation increases in line with increasing oxidation rate toward the surface.

Table III presents data for the change in physical properties of the impregnated rods upon gasification to essentially constant burn-off, with one exception the burn-offs falling between 10.7 and 11.9%\*. The specific surface areas are found to be markedly increased upon gasification, as shown previously<sup>6</sup>. The surface area developed in the unimpregnated rods is found to increase with increasing reaction temperature over the range 900–1100°C, in line with previous findings and explanations involving the physical structure of graphitized carbon rods<sup>11</sup>. This increase in area developed with increasing reaction temperature for rod<sub>0</sub> parallels the increase in helium density, suggesting that, at least in part, the increase is caused by opening up closed pore volume. If also the increase in area with increasing reaction temperature is interpreted as meaning that a continually higher percentage of binder (being more activable) is reacted<sup>11</sup>, the conclusion is made that the majority of the original closed pore area is located in the binder. The essentially constant apparent density and open porosity produced in rod<sub>0</sub> after gasification at different temperature is in line with only a slight change in external sample diameter occurring upon reaction.

\*In some instances, the variation in burn-off affects the quantitative relationship of some of the data in Table III, but does not affect the qualitative trends which the data are meant to show.

TABLE III  
*Changes in Physical Properties of Impregnated Rods upon Gasification to Essentially Constant Burn-off*

Reaction temp., °C	Burn-off %	Specific surface area, m <sup>2</sup> /g	Helium density, g/ml	Apparent density g/ml	Open porosity %	Macroporosity in total open porosity %
Unimpregnated						
Unreacted	—	0.31	2.110	1.641	22.2	91.5
900	10.8	1.45	2.161	1.482	31.4	91.4
1000	10.7	1.51	2.183	1.499	31.4	84.2
1100	11.3	3.59	2.195	1.497	31.8	77.8
3 Impregnations						
Unreacted	—	0.18	2.030	1.746	14.0	89.2
900	13.5	(1.67)*	2.129	1.559	26.7	92.3
1000	10.8	1.31	2.109	1.601	24.1	91.2
1100	11.8	(1.66)†	2.099	1.622	22.7	93.0
7 Impregnations						
Unreacted	—	0.13	1.962	1.821	7.2	98.1
900	11.9	1.92	2.112	1.624	23.2	93.7
1000	11.8	1.45	2.095	1.628	22.3	92.9
1100	11.6	1.28	2.076	1.672	19.4	94.5
12 Impregnations						
Unreacted	—	0.09	2.033	1.865	8.3	67.8
900	10.9	1.17	2.103	1.683	20.0	92.8
1000	11.1	1.08	2.092	1.690	19.3	92.1
1100	11.5	0.99	2.083	1.748	16.1	95.3

\* This surface area value is undoubtedly too high because of excessive burn-off. In line with the findings for rod<sub>3</sub> reacted at 1100°C, the surface area for ca. 10.6% burn-off can be estimated at ca. 1.0 m<sup>2</sup>/g.

† A second sample was reacted to 10.6% burn-off, and the surface area was 1.36 m<sup>2</sup>/g.

The results in Table III for the impregnated samples can be systematically explained, if the surface area produced upon gasification of rod<sub>3</sub> at 900°C is disregarded, because of excessive burn-off variation. Following the reasoning of Walker and Raats<sup>11</sup>, the surface area developed at a constant burn-off increases with increasing gasification temperature until the diffusion rate of the reactant gas between particles is not sufficiently rapid to supply gas to all the interior of the sample. As the degree of impregnation is increased, the diffusion rate of reactant gas is decreased; and the temperature at which the developed area goes through a maximum also decreases. It is seen in the present case

that with three impregnations the diffusion rate is not sufficiently decreased to prevent maximum area development at the maximum reaction temperature, even though the amount of area increase with increasing reaction temperature is considerably less than for the unimpregnated samples. On the other hand, for seven and twelve impregnations, the diffusion rate has been sufficiently decreased to cause maximum area development at the lowest reaction temperature studied.

For the impregnated samples, the helium densities decrease and open porosities increase upon gasification, as expected. The apparent densities in all cases increase with increasing

gasification temperature in line with the greatest decrease in external sample volume occurring at the maximum gasification temperature. The same reasoning can be applied to the porosity data.

Figures 3 through 6 present data on the

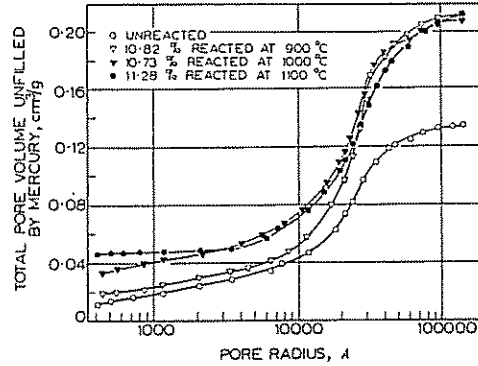


Fig. 3. Change in open macropore volume-distribution in unimpregnated rods with "constant" burn-off at different temperatures.

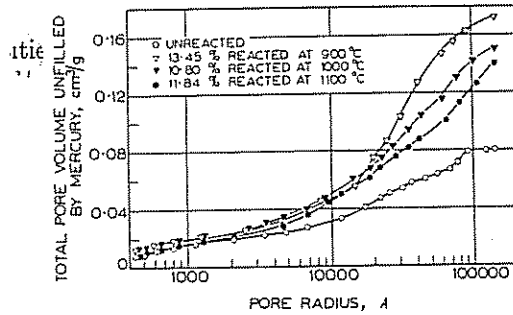


Fig. 4. Change in open macropore volume-distribution in rods impregnated three times with "constant" burn-off at different temperatures.

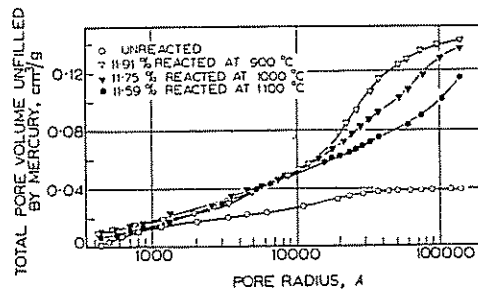


Fig. 5. Change in open macropore volume-distribution in rods impregnated seven times with "constant" burn-off at different temperatures.

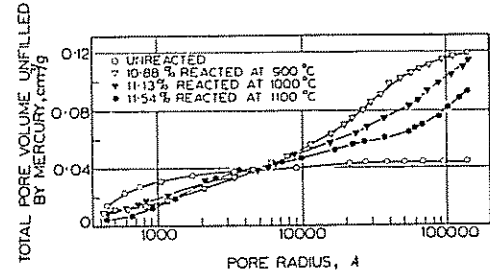


Fig. 6. Change in open macropore volume-distribution in rods impregnated twelve times with "constant" burn-off at different temperatures.

macropore distribution in the rods before and after gasification. From these data the percentage macroporosity in the total open porosity can be calculated, as given in Table III. For the unimpregnated samples there is a decrease in per cent macroporosity, which qualitatively parallels an increase in surface area, as would be expected. For the impregnated samples, nothing of particular interest happens to the percentage macroporosity, except for the unreacted rod<sub>12</sub>, which has been previously discussed.

The curves in Figs. 3 through 6 warrant some additional discussion. It is observed that the total open pore volume created after gasification of the unimpregnated rods is essentially reaction-temperature independent, which is in line with the rather uniform reaction of the binder through the rods at each temperature. On the other hand, with the unimpregnated samples, the total open pore volume created decreases with increasing reaction temperature. This is consistent with a decreasing percentage of binder and impregnant reacting as temperature is increased. Indeed, observation of the close proximity of shape of the macropore distribution-curves for the impregnated samples reacted at 900°C to that of the original, unimpregnated sample clearly shows the preferential reaction of the impregnant material from the samples, leaving a carbon skeleton similar to that in the original rod.

Again looking at the distribution curves in Fig. 3 for the unimpregnated rods, it is

interesting to note that as the specific micropore volume of the rods increases the rod's helium density also increases. To account for the helium density of rod<sub>0</sub> increasing from 2.110 to 2.195 g/ml upon gasification at 1100°C, it is calculated that 0.019 ml/g of closed pore volume was opened up. This may be compared to the 0.0356 ml/g increase in microporosity upon gasification at 1100°C, as seen in Fig. 3, and indicates that this microporosity increase upon gasification was caused by enlarging the volume of previously open micropores and/or starting new ones in addition to unblocking previously closed micropores.

In Fig. 6, it is seen that the reacted samples of rod<sub>12</sub> have lower microporosities than the unreacted rod. This can probably be explained in line with the non-uniformity of micropore distribution in rod<sub>12</sub>, as discussed in conjunction with Fig. 2. As the external diameter of the sample is decreased by reaction, microporosity would be decreased solely in line with the decrease in microporosity with decrease in sample diameter, as observed in Fig. 2.

#### B. Effect of Impregnation on Gasification Rates of Rods with Carbon Dioxide

Rods were reacted with carbon dioxide at 900, 1000 and 1100°C up to 13.5% burn-off. Typical curves<sup>6, 11</sup> showing an increasing reaction rate with time up to ca. 5% burn-off and then a constant rate, when expressed as g/hr reacting, were found. Table IV presents the rate data as a function of tem-

TABLE IV

*Effect of Impregnation on Gasification Rates of Rods with Carbon Dioxide*

Number of Impregnations	Reaction rate g/hr/g of starting material			Over-all activation energy kcal/mol
	900°C	1000°C	1100°C	
0	0.013	0.058	0.17	43
3	0.010	0.072	0.29	55
7	0.011	0.070	0.24	51
12	0.013	0.070	0.22	47

perature and number of impregnations.

At 900°C, it is seen that the reactivity of the rod<sub>0</sub> is essentially the same as that of the impregnated rods. The two major differences in properties of these rods, surface area and presence of impregnant, have counterbalancing effects on reactivity. The amorphous impregnant in rods<sub>3, 7 and 12</sub> would be expected to react more rapidly than the original graphitized skeleton, and there is a slight increase in reactivity at 900°C with increasing impregnation. On the other hand, the considerably higher surface area of rod<sub>0</sub> would cause it to have a higher reactivity than the impregnated samples. If the reaction rate results at 900°C be expressed on the basis of starting surface area, the reactivity of rod<sub>12</sub> is ca. three times as high as rod<sub>0</sub>, giving an indication of the higher reactivity of the impregnant.

Looking at the impregnated samples as reaction temperature is increased, it is seen that the reactivity increases less rapidly (lower activation energy) the greater  $t^{1/2}$  degree of impregnation. This can be explained<sup>15</sup> as resulting from a decrease in the rate of gas transport within the rods with increasing impregnation and an accompanying increase of control of the reaction by internal diffusion. The result, as shown<sup>15</sup>, is a reaction with decreasing over-all activation energy.

The fact that the unimpregnated rods show the lowest activation energy and yet have the highest rate of internal gas transport can again be explained on the basis of two opposing trends. Even though the higher gas diffusion rate through rod<sub>0</sub> should in itself result in a higher activation energy for the reaction, this is offset by its having the greatest initial internal area to be utilized. That is, a completely non-porous body where reaction occurs entirely on the surface would show the highest activation energy for

<sup>15</sup> P. L. Walker, Jr. and Emile Raats, *J. Phys. Chem.* **60**, 370 (1956).



its reaction even though the rate of internal gas transport would be zero. On the other hand, a body of high surface area and high internal gas diffusion rate can show a low activation energy because of the decrease of its area being exposed to unit gas concentration as reaction temperature increases. The two effects tend to counterbalance each other, with the dominating effect being determined by the differences in internal gas diffusion rate and starting surface area for various samples.

C. *Effect of Impregnation and Subsequent Burn-off on Electrical Resistivities of Rods*

Table V presents the electrical resistivity

TABLE V  
*Effect of Impregnation and Subsequent Burn-Off at Different Temperatures on the Electrical Resistivity of Rods*

Number of impregnations	Resistivity, $\Omega\text{cm} \times 10^2$			
	unreacted	900°C	1000°C	1100°C
0	0.75	1.19	1.05	1.05
3	0.78	1.08	1.05	1.02
7	0.81	1.02	1.02	0.96
12	0.72	0.87	0.87	0.84

data (determined at room temperature) on samples before and after "constant" burn-off (ca. 11.5%) at different temperatures. The greater resistivity of unreacted rods<sub>3</sub> and <sub>7</sub> over rod<sub>0</sub> is noted with surprise. The resistivity values can be duplicated within 1%; and, therefore, the differences are meaningful. Furthermore, the same trend was found on three different sets of samples\*. On the other hand, the resistivity of rod<sub>12</sub>

\* Mr. Cory, Graphite Specialties Corporation, always finds a slight decrease in resistivity upon impregnating a graphitized carbon rod with amorphous material. Therefore, at the moment, the authors are reporting the above results for information and will not discuss the possible reasons for them until they are confirmed on additional samples of impregnated rods treated in different ways. Suffice it to say that impregnation of a graphite skeleton with amorphous impregnant has little effect on electrical resistivity.

is less than rod<sub>0</sub>, which is in line with what would be ordinarily expected. The trend of decreasing resistivity with increasing impregnation after burn-off at a constant reaction temperature is as expected. As impregnation is increased the percentage of filler and initial binder material reacted away at constant burn-off is decreased. Since this material is primarily the conducting phase, the higher the percentage of this material in the final rod the lower the resistivity. For a given number of impregnations, the resistivity is found to increase as reaction temperature decreases. This is in line with a greater uniformity of reaction through the rod (through the impregnant, binder, and filler material) the lower the reaction temperature. This would result in the lowest reaction temperature producing a reacted rod of lowest percentage of filler and, consequently, the highest resistivity.

D. *Effect of Impregnation on the Effective Diffusion Coefficients of Hydrogen-Nitrogen through the Rods*

From Table VI, it is seen that the effective diffusion coefficients of hydrogen-nitrogen through the rods decrease markedly with impregnation up to seven times. This is, of course, due to the filling of macropore voids between particles which exist in the original rods. Some anisotropy of diffusion is observed, as was discussed previously<sup>16</sup>.

There is some doubt as to the magnitude of the diffusion coefficients for rods<sub>7</sub> and <sub>12</sub>. That is, the more impervious a sample becomes the greater the error introduced by leakage of gas around the sides of the sample. Weisz<sup>17</sup> reports that, for the apparatus used to determine  $D_{eff}$ , glass plugs are found to have a value of 0.0002 cm<sup>2</sup>/sec. This is considerably less than the values reported for rods<sub>7</sub> and <sub>12</sub> and suggests either that there is

<sup>16</sup> P. L. Walker, Jr., Frank Rusinko and Emile Raats, *Nature* 176, 1167 (1955).

<sup>17</sup> Private communication from P. B. Weisz (1956).

TABLE VI  
*Effect of Impregnation on the Effective Diffusion Coefficients of  
 Hydrogen-Nitrogen Through the Rods*

Number of impregnations	$D_{eff}$ , cm <sup>2</sup> /sec		$D_{eff}$ Ratio
	⊥ to extrusion	∥ to extrusion	
0	0.0135 ± 0.0006 (4)*	0.0148 ± 0.0006 (5)	1.10
3	0.0045 ± 0.0002 (4)	0.0066 ± 0.0003 (3)	1.47
7	0.00146 ± 0.00005 (5)	0.00227 ± 0.00021 (5)	1.55
12	0.00160 ± 0.00017 (5)	0.00207 ± 0.00010 (5)	1.30

\* Number of samples run.

some connected internal porosity in these rods through which gas diffusion occurs or that more leakage of gas occurs around the sides of the carbon samples than the glass cylinders because of greater surface roughness. Indeed, even the fact that  $D_{eff}$  parallel to extrusion is greater than that perpendicular for rods<sub>7</sub> and <sub>12</sub> could be caused by the difference in channeling effect of the surface roughness.

#### IV. CONCLUSIONS

Impregnation of graphitized carbon rods with an amorphous material which is then only carbonized is found to markedly decrease the rate of gas diffusion through the rods. Little else is gained by such impregna-

tion (with the possible exception of strength, which has not been investigated). Reactivity to an oxidizing gas, expressed per unit sample volume, is essentially unchanged or increased, depending upon the reaction temperature. Electrical resistivity is essentially unchanged. Probably the resistance to thermal shock is decreased in line with decrease in internal porosity,<sup>18</sup> even though this fact has not been checked.

The authors wish to thank P. B. Weigert (Socony-Mobil Laboratories) for determining the diffusion data and for his continued interest in this work.

<sup>18</sup> F. A. Hummel, *Ceram. Ind.* **65**, 73 (1955).