

## Aspects of the Reactivity of Porous Carbons with Carbon Dioxide

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### I. Introduction

This work was undertaken in order to develop a simple and effective test that would compare the reactivities of granular carbons. The carbons studied were samples of formed metallurgical coke and of calcined coal char made from subbituminous coal in the process developed by FMC Corp., and demonstrated in a semi works plant at Kemmerer, Wyoming (1). This coke is permeated by a system of very fine pores, it has a highly amorphous solid structure, and it is very reactive compared to byproduct or beehive cokes. The reactivity is believed to be an important property of cokes used as reducing agents.

As a second objective, some knowledge of the influence of rather mild thermal treatment on the reactivity of these cokes was sought.

Carbon dioxide was selected as the oxidizing agent for the reactivity tests, since its reaction with carbon is not complicated by secondary effects such as the water gas shift. The reaction was followed by measuring the weight of carbon as a function of time, and this procedure proved to be both simple and precise.

While the variables affecting the results of the test were studied in a semi-empirical manner, certain interesting information regarding the kinetic behavior of these carbons as they underwent reaction did result, and this work is presented with the hope of providing a lead toward a better picture of what happens on the surface of carbon during reaction.

### II. Experimental Details

#### A. Reactivity Measurements

The apparatus shown in Figure 1 consisted of an impervious silica tube 2.54 cm. I D mounted vertically in a tube furnace. Carbon dioxide flowed upward through the tube at controlled rates which ranged from 2870 cc per minute (STP) to 4730 cc per minute. The samples of granular carbon to be evaluated were suspended in a sample holder from an analytical balance mounted above the reaction tube. The sample holder was a No. 2 Gooch crucible cut off where the outside diameter was 23 millimeters so that clearance between the crucible and the reaction tube averaged 1.2 mm. The perforations in the bottom of the crucible were each .7 mm Diam. Holes were cut in the sides of the crucible with a diamond saw so that a bale of quartz fiber which hooked on to another long quartz fiber attached the sample holder to the balance.

Nearly all of the reactivity measurements were made at 900°C and the temperature was controlled automatically by the thermocouple mounted about 1 cm below the sample. At 900°C, the rates of reaction of most of these samples were in a range that was convenient to follow.

A loose fitting cover on top of the reaction tube with a small hole for the quartz fiber prevented air from diffusing down to the sample yet permitted the CO<sub>2</sub> to escape.

The dynamic force or upward drag on the sample basket was about 50 milligrams at the highest gas velocity used, and it was steady as long as gas velocity and temperature were kept constant.

To make a reactivity measurement the carbon particles were screened, usually to -16 +20 USS mesh, dried overnight in a desiccator and a sample of either 200 or 500 milligrams was weighed into the sample holder. With the apparatus at reaction temperature and thoroughly purged with nitrogen, the sample holder was quickly lowered into place, hung from the balance, and the cover placed on top of the reaction tube.

The sample was then allowed to heat in a stream of nitrogen until it came to a constant weight, which usually happened within ten minutes, but for most runs a 20 minute devolatilization period was used. At the end of this time the weight was observed, the carbon dioxide was turned on and its flow adjusted to give a superficial velocity of either 15.6 or 9.45 centimeters per second (STP) in the reaction tube. The weight was again measured as soon as possible after turning on the CO<sub>2</sub> and thereafter at frequent intervals during the course of the reaction. At the end of the run the system was purged with nitrogen, and the sample was removed and allowed to cool to room temperature. The empty sample holder was then placed back in the furnace and weighed in a stream of nitrogen at reaction temperature. Reactivities are reported as percent of the sample reacting per hour, based on the total weight (including ash) of carbon at the end of the devolatilization period.

For most of the work the lower gas velocity, 9.45 cm/sec, was used because it gave somewhat more reproducible results. At this velocity, the Reynolds Number in the annular space past the sample is 900, so that flow is laminar.

## B. Fluidized Reactor

The apparatus to react carbon with steam in a fluidized bed consisted of an impervious silica tube 2.54 cm I D mounted vertically in a furnace. The heated section of the tube was 45 cm long, and it contained refractory packing to a depth of 25 cm to preheat the steam. A perforated porcelain plate pinched into a constricted section of the tube lay on top of the packing and served as a grid. A thermocouple in a fine quartz well was immersed in the bed from the top, and it operated a controller which acted to maintain a constant temperature in the bed.

The rate of steam flow was controlled by manual adjustment of the current to a heating mantle enclosing a two liter flask. The flask was filled to a level well above the windings in the mantle.

To begin a run, the empty reaction tube was weighed, then mounted in the furnace, brought up to temperature, and the steam flow was adjusted to the proper rate. The weighed carbon sample (20 grams) was then poured into the tube, and a plug of glass wool was inserted into the top. By proper manipulation of the heater, the bed temperature reached the desired value (usually 750°C) within 5 minutes.

Coarse carbons, -6 +10 USS mesh, were used for this work. At a superficial steam velocity of 25 cm/sec under reaction conditions, particles in the bed moved

about continuously. Thus each particle should have been exposed to the same conditions. The beds were about 5 cm deep.

#### C. Surface Area Measurements

A Perkin-Elmer-Shell Sorptometer (Model 212) was used to measure pore surfaces. Samples were degassed in the apparatus at 600°C under .1 mm Hg for 30 minutes.

Isotherms for adsorption of nitrogen at 78°K were obtained by a flow technique which is rapid, but which may not allow sufficient time for equilibrium to be attained in very fine pores. Thus the surface areas reported here may be somewhat low.

#### D. Particle Density and Pore Volumes

Particle densities or volumes were measured by displacement of Hg at 10 psig in an American Instrument Co. Porosimeter. Pressures to 5000 psi enabled pore volume distributions to be determined down to pore diameters of 350A.

#### E. Helium Densities

Helium density was measured in a Beckman purgeable gas pycnometer, after degassing in the apparatus at room temperature and .1 mm Hg twice for about 10 minutes each time, and breaking the vacuum with He in each case.

#### F. Heat Treatment of the Samples

To study the effect of heat treatment on reactivity the carbons were soaked for various periods of time in a muffle furnace kept at either 1000°C or 1100°C. During this soaking, whole briquets were contained in glazed porcelain crucibles with calcined coal packed around them and with covers on the crucibles.

### III. Samples

Two samples of FMC Coke briquets and one sample of calcined coal char were studied in this work.

The coke briquets were made in pilot scale equipment by first calcining the ground coal in a series of fluidized retorts, then briquetting the devolatilized coal or calcinate with a binder made by air blowing the tar distilled from the coal. The green briquets were then cured in the presence of air to polymerize the binder, and were finally coked or baked at about 900°C.

One sample of coke was made from Elkol Coal, a sub-bituminous coal mined near Kemmerer, Wyoming. The other coke was from another sub-bituminous coal mined near Helper, Utah.

For the samples used here, coke briquets were crushed and screened to the desired size.

The sample of calcinate was made from Elkol Coal and was produced by FMC Corp's demonstration plant at Kemmerer, Wyoming. The pulverized coal was first dried at 150°C, then carbonized at 450°C, and finally calcined at 800°C in a series of fluidized retorts.

Properties of these carbons are given in Table I.

TABLE I  
Properties of Samples

	<u>Elkol Coke</u>	<u>Helper Coke</u>	<u>Elkol Calcinate</u> <sup>***</sup>
Ultimate Analysis			
Wt. % C	89.8	86.6	89.6
H	1.0	1.0	1.3
N	1.0	1.2	1.2
S	.6	.3	.4
O (by diff.)	1.7	2.6	1.7
Ash	5.9	8.3	5.8
Volatile matter %	2.0%	2.0%	4.5%
Surface area (m <sup>2</sup> /gm) BET-Nitrogen	240*	170	190
Apparent density by Hg displacement (gm/cc)	.94	.96	.94
Helium density (gm/cc)			1.98
Crushing strength of cylinders 1-1/4" x 3/4"	3400#	3400#	

\*190 m<sup>2</sup>/gm is a typical surface area for the coke produced by the large-scale plant at Kemmerer.

\*\*\*The Elkol Coke used here was not made from this sample of calcinate.

#### IV. Results

##### A. Effects of Procedure

Several of the possible variables of this apparatus were studied to determine their effects on the reactivity measurements and to establish a standard procedure. The Elkol coke was used for this aspect of the work.

The numerical rates or reactivities reported in this section are based on the overall slope of the weight versus time curve between the times of 30 and 160 minutes where the slope was fairly constant. In the first few minutes of reaction, rates were somewhat higher than the slope in this interval, and the possible significance of this higher initial rate is discussed in a later section.

Table II shows the effects of sample size, devolatilization time, gas velocity, and particle size on the measured values of reactivity. In brief, increasing the sample size from 200 to 500 milligrams decreased the reactivity about 20%; longer devolatilization times (40 compared to 20 minutes) decreased the reactivity roughly 10%; and decreasing the gas velocity from 15.6 to 9.45 centimeters per second lowered the reactivity about 20%. Particle size between -6+10 and -28+32 mesh had no appreciable effect. (These screen sizes cover a five fold range of average particle size, from 2.5 down to .5 millimeters.)

TABLE II  
Variables Affecting Reaction Rate\*

Particle Size	Heating time min.	Sample Wt. mg.	Gas Velocity cm/sec	Reaction Rate %/hr	Comparison of Variables
-16+20	20	200	15.6	25.6 25.1 26.4	
		500		20.1 21.4 20.2	
	40	200		24.1 24.1	
		500		18.3 18.4	
	20		9.45 9.15	17.6 17.2	
- 6+10			9.45	17.8 17.7 18.2	
-16+20				17.6	
-28+32				17.8 17.9	

\*(Elkol Coke)

The procedure adopted as standard used the -16+20 mesh size range, a heating time of 20 minutes, 500 mg. of sample and a gas velocity of 9.45 cm/sec. Reproducibility under these conditions was good, as can be seen from Table II.

The reactivity was reproduced with several different sample baskets made as described above, but having slightly different wall clearances. Thus the dimensions of the sample holder are not critical.

#### B. Effects of Carbon Monoxide

It is well known that CO and H<sub>2</sub> retard the reaction between CO<sub>2</sub> and carbon (2,3). With the sample sizes and flows of CO<sub>2</sub> that were used here, the average concentration of CO generated in the reactivity apparatus was usually between .1 and .2% (i.e. moles CO produced/unit time divided by moles of CO<sub>2</sub> fed/unit time). For the most reactive sample, the composition of CO in the effluent gas was about .45%.

Several runs with CO added to the CO<sub>2</sub> fed to the reactor (total flow kept constant) showed the rate to be lowered about 20% with 3.7% CO in the gas. This is about what Ergun's data (4) would predict and it shows that the CO generated by reaction should have a very minor influence on the measured values of reactivity.

### C. Heat Treatment

Figures 2, 3, 4, and 5 show how the weights of carbon samples changed with time during reactivity determinations. Note that zero time has been shifted for most of the data on Figures 3, 4, and 5 so that several runs can conveniently be compared on a single plot.

From these plots, two results are apparent. First, as would be expected, a more severe heat treatment causes a given carbon to react more slowly.

Secondly, the heat treatment causes the rate of reaction to become more nearly constant, during a particular run. In Figure 2, for example, a sample of Helper coke which had been soaked at 1000°C for 16 hours reacted at very nearly a constant rate until more than 56% of the carbon had been consumed. The least-squares slope of this line to 56% burn off gives a reactivity of 38.1%/hr with 95% confidence limits of  $\pm 5.1\%$ /hr. The other sample in Figure 2 was soaked for 27 hours at 1000°C and it reacted to 57% burnoff at a constant rate of  $24.7 \pm 2.28\%$ /hr. The 95% confidence limits give a quantitative idea of how nearly constant these reaction rates were.

### D. Effect of Temperature

Except for two runs at 850°C all of the reactivities reported here were measured at 900°C. The two runs at 850° with Elkol coke gave reactivities of 6.5 and 7.1% per hour and when compared with 17.8% per hour at 900°C the apparent overall activation energies were 58.3 and 56.0 K cal per mole, respectively.

### E. Variation of Pore Surface with Burnoff

Pore surface areas and particle densities were determined for 500 mg samples of Elkol calcinate which had reacted with CO<sub>2</sub> for various lengths of time in the reactivity apparatus. The first part of Table III shows these data. This carbon had been heated only to 800°C before undergoing reaction, so that the rate of reaction decreased continuously with burnoff, as was the case for the "un-heat-treated" carbon in Figure 5.

The specific surface of the carbon increased more or less continuously with burnoff, but when the surface area was based on 1 gram of original sample, before reaction (Column 6), it went through a maximum at about 35% burnoff. The data, plotted in Figure 6, show that the surface of a sample rises rapidly to a maximum and then falls off as carbon is consumed. Probably, during the initial stages of reaction, additional pore surface is very quickly made available by erosion of constrictions, and perhaps by enlargement of very fine pores. However, during the later part of the reaction, beyond 35 to 40% burnoff, pore surface is destroyed more rapidly than it is created, most likely by consumption of walls separating fine pores.

It is conceivable that the actual surface accessible to the carbon dioxide or steam at reaction conditions differs greatly from that measured by adsorption of nitrogen at 78°K. However, it is hard to imagine that the pore surface available to the reactant gas can do anything but increase during the first 10 to 20% of burnoff. During this part of the reaction, the rate either remains essentially constant, or decreases gradually.

Thus during the course of reaction of a particular sample of carbon there seems to be no correlation between reaction rate and pore surface area.

The percent internal reaction from the last column in Table III gives the weight loss calculated from the particle densities, which assumes that all reaction takes place on the internal pore surface. The difference between this figure and the actual weight

TABLE III  
Variation of Pore Surface with Burnoff

Time Reacted Min.	Overall Wt. Loss %	Particle Density gm/cc	Overall Rate %/hr	Specific Surface m <sup>2</sup> /gm	Surface* Per Gm. Starting Material m <sup>2</sup> /gm	Internal Reaction** %
Calcined Elkol Coal -20+30 Mesh Reacted with CO <sub>2</sub> in Reactivity Apparatus at 900°C						
0	0	.935		190	190	
15	5.7	.934	20.7	453	430	
30	10.0	-	20.0	592	534	
45	13.9	.815	18.5	642	552	12.8
60	18.2	.765	18.2	760	622	18.2
75	21.8	.721	17.4	790	616	22.9
90	25.9	.737	17.3	930	689	21.2
105	27.4	.681	15.7	975	707	27.1
120	32.0	.686	16.0	982	668	26.6
135	34.8	.655	13.9	1165	770	30.0
150	40.7	.639	16.2	1180	700	31.7
165	41.2	.605	15.0	1229	721	35.3
180	44.1	.625	14.7	1158	646	33.1
210	44.5	.618	12.7	1108	615	33.8
240	58.9	.530	14.7	1501	616	43.3
270	60.2	.510	13.4	1581	625	45.5
300	63.1	.549	12.6	1426	526	41.3

Calcined Elkol Coal -6+10 Mesh Reacted with Steam in Fluid Bed at 750°C

0	0	.965		139	139	
30	8.0	.908	16.0	560	515	5.9
45	13.0	.873	17.4	559	485	9.5
60	20.0	.817	20.0	743	596	15.2
75	23.5	.835	18.8	801	612	13.5
75	21.5	.767	17.2	798	628	20.5
90	26.5	.702	17.7	792	583	27.1
90	28.5	.760	19.0	784	561	21.1
105	34.5	.649	19.7	942	619	32.7
105	32.5	.711	18.6	899	608	26.1
105	33.5	.731	19.2	830	552	24.1
120	35.0	.693	17.5	911	592	28.1
120	37.5	.678	18.8	712	445	29.7
135	43.5	.579	19.3	893	504	40.0
135	43.0	.645	19.1	933	532	33.1
150	48.0	.586	19.2	911	475	39.2
150	45.0	.588	18.0	968	532	39.0
165	51.2	.615	18.6	907	442	36.2
165	49.9	.494	18.1	1100	551	38.8
180	55.5	.527	18.5	964	429	35.4
180	52.0	.567	17.3	1064	511	41.3
180	56.6	.589	18.9	945	409	39.0
180	51.5	.552	17.2	942	457	42.8

\* (Specific Surface) (100 - % wt. loss)/100

\*\* 1 - (part. density)/(initial part. density)

loss represents carbon consumed on the outsides of the particles. Although the data are somewhat erratic, roughly 85% of the reaction took place on the internal surface up to 40% burnoff.

The second set of data in Table III refers to -6+10 mesh Elkol calcinate reacted with steam at 750°C in the fluidized bed. Here, at a lower temperature, the rate of reaction of "un-heat-treated carbon" is very nearly constant at 18.2%/hr with 95% confidence limits of  $\pm 1.0\%$ /hr. (These measurements are less precise.) In this case also, the pore surface increases to a maximum at about 30% weight loss, and then decreases. Since there is some attrition in the fluid bed, particularly at high burnoff, the amount of internal reaction is quite a bit less than that indicated by the actual weight loss.

## V. Discussion

### A. Variables affecting reactivity

Several observations indicate that mass transfer is not a major factor limiting the rate of reaction in this work. First, the fact that a five fold range of particle sizes had no apparent influence argues that diffusion within the pores of the particles and diffusion from the voids in the sample bed to the surface of the particles did not cause a significant concentration gradient, and that therefore, the concentrations of carbon dioxide and carbon monoxide in the voids between particles must be essentially the same as at the pore surfaces where reaction takes place.

Second, the overall activation energy of 56 to 58 K cal is too large for diffusion to the particles to control the rate, even though this activation energy was determined between only two temperatures, and most of the data pertain to the higher temperature.

Another factor which suggests that external or film diffusion does not govern the rate is that the observed rates of reaction varied from 70% per hour to 4% per hour depending only upon the characteristics of the carbon. Thus, over this range of reactivities any effects on the diffusion rate to and from the particles by the geometry of the apparatus or the pattern of gas flow should have been unchanged.

Although diffusion of gas either to the particles or within their pores does not appear to strongly affect the rate of reaction here, its effect may not be negligible, particularly at the higher rates. If film diffusion, pore diffusion, and chemical reaction at the pore surface are regarded as three resistances to reaction arranged in series, lowering one resistance, as when the pore surface becomes more reactive, increases the relative significance of the others.

The importance of pore diffusion is undoubtedly affected by the pore structure. If a carbon is very dense, and has only very fine pores, its permeability to the reactant gas may very well be so low that reaction only takes place near the external surface of the particles. Thus the pore structure (permeability as well as pore surface area) might very well influence measured values of reactivity in this apparatus.

A further, and most likely the predominant, physical factor influencing the values of these reaction rates is that the samples were probably not isothermal. At a rate of 20% per hour, the endothermic reaction of carbon dioxide requires about 360 calories per hour for a 1/2 gram of carbon. Assuming that this heat is transferred principally by radiation, the surface of the sample was probably 2° to 4°C less than the measured temperature inside the reaction tube. With an activation energy of 58 K cal such a difference in temperature would lower the rate by a factor of 4 to 8%. This cooling effect would be more pronounced with the larger samples and at the lower gas

velocities. Therefore, the actual sample temperature and thus the measured reaction rate would be somewhat lower for larger samples and lower gas flows, as was observed.

The net result of all of these factors is that while this procedure does indicate significant differences in reactivity among various samples of carbon, the measured values are somewhat compressed. At the higher rates of reaction the combined retarding effects of diffusion, carbon monoxide, and a somewhat lowered sample temperature give a measured value of the reactivity which is less than would be the case if the sample were reacting under the same actual conditions as one with a lower reactivity. At the lower rates of reaction these inhibiting influences are not so large since concentration differences between the sample and the main stream of the gas are less, as are temperature differences. Thus these differing values of reactivity must be interpreted as occurring under conditions of reaction which are not exactly similar and where the higher rates have taken place under "slower" conditions so that the true differences in reactivity are actually somewhat greater than those reported here.

### B. Concentration Gradient Inside Particles

Since, with the Elkol Coke, variation of particle size from about 2.5 to .5 mm did not influence the measured reactivity, one might conclude that reaction occurred entirely within Zone I (5) - that is uniformly throughout the particles, with a negligible radial gradient in the concentration of  $\text{CO}_2$ .

However, the particle densities reported in Table III for Elkol calcinate show the percent of internal reaction to be consistently less than the overall weight loss, which suggests that reaction is not uniform throughout the particle.

In the case of Elkol calcinate, macro-pore volume measurements by displacement of Hg up to 5000 psi show a porosity of 28% in pores larger than 350A in diam. About two-thirds of this porosity is in pore sizes between 3000 and 30,000A. If these large pores are regarded as arteries which conduct gas to cells where the pores are much finer (the mean diameter of the pores less than 350A diam. is 25 to 30A), it should be possible to estimate whether a significant radial concentration gradient occurs in these pores.

From density profiles of carbon rods exposed to  $\text{CO}_2$  for various times at several temperatures, Walker and co-workers (6,7) concluded that the dimensionless group  $\left(\frac{R}{C_R \text{ Deff}}\right) \left(\frac{dn}{dt}\right)$  is a measure of whether reaction occurs uniformly throughout the particle in Zone I, or Zone II where the  $\text{CO}_2$  is all consumed before it can diffuse to the center of a particle. Here R is the particle radius;  $C_R$  the reactant concentration in the main stream;  $dn/dt$  the overall reaction rate per unit particle external surface; and Deff the effective diffusion coefficient of  $\text{CO}_2$  within the particle, all these terms being in consistent units. Deff equals  $D \epsilon / \gamma$ , where D is the diffusion coefficient in a single cylindrical pore;  $\gamma$ , the tortuosity factor (estimated at 20); and  $\epsilon$  the fraction of the external particle surface covered with pore openings - estimated to be 1/3 the volume porosity for pores 3000 to 30,000 A in diam.

Assuming spherical particles, a first order reaction, and no inhibition by products, if  $(R/C_R \text{ Deff}) (dn/dt)$  is less than .03, reaction should be in Zone I; if greater than 6.0, the conditions of Zone II apply.

Using data from Table III and 3000 A for "large" pore diameters, estimates of this dimensionless group vary from .8 to 2.4, which indicates that while reaction occurs throughout a particle, it does so to a greater extent close to the external surface -- that is, the condition is between Zones I and II.

A question remains concerning the "cells" of fine pores surrounded by the network of large arterial channels. If the dimensionless group  $\left(\frac{R}{C_R \text{ Deff}}\right) \left(\frac{dn}{dt}\right)$  is set equal

to .03, which is its maximum value if the conditions of Zone I (uniform reaction) apply, the equality can be solved for R, the maximum particle or "cell" radius for uniform reaction. Estimating values for  $C_R$ ,  $Deff$  (Knudsen diffusion occurs in pores 25A diameter) and  $dn/dt$  (a function of R), and solving for R gives a value of .014 cm for the calcinate used in the first part of Table III. This gives a "cell" diameter which is about half a particle diameter. Since a "cell" of this size must surely be permeated by the large pores, it is the concentration gradients in the large arterial pores which must be responsible for non-uniform reaction.

### C. The Constant Rate of Reaction

Figures 2, 3, 4, and 5 show that for heat treated carbons, the weight-time plot during a considerable portion of reaction is very close to a straight line.

The fact that the kinetic order of carbon can be zero after 1 or 2% burnoff has often been observed before (8,9). The carbons discussed here were all exposed to some  $CO_2$  or steam at  $800^\circ-900^\circ C$  in their preparation, so this initial burnoff undoubtedly occurred prior to these reactivity measurements.

It is of particular interest to note that while the reaction rate is either constant or slowly decreasing, the pore surface first rises rapidly, and then decreases. The data for Ekol Calcinate of Table III are plotted in Figure 6.

Forty years ago, Chaney and co-workers established that the pore surface as manifested by adsorptive capacity for vapors first rises to a maximum and then falls off as a given sample of carbon undergoes activation (10).

Thus there is apparently no relation between a carbon's pore surface area and its rate of reaction with  $CO_2$  or steam as a particular sample undergoes reaction. Even though pores may be available to the reacting gas at  $750^\circ-900^\circ C$  which are not coated by nitrogen at low temperature in the surface area determinations, the extent of pore surface and its accessibility must certainly increase during the first 10 to 20% of reaction.

With the available surface changing as it does, the constancy of the reaction rate of these stabilized carbons is particularly striking. The explanation of a constant "porosity profile", which might well apply under conditions of Zone II (6) does not seem to apply here, where reaction is occurring throughout the particles.

In the reaction mechanism set forth by Ergun (11) an oxygen atom adsorbed on the carbon surface goes off as carbon monoxide and leaves behind either one, two or no active sites on the carbon. In the present case a single active site must be left behind on the stabilized carbon to give a rate of reaction so nearly constant. This constant rate is strong evidence that for a carbon stabilized by heat treatment, reaction of a molecule of  $CO_2$  or  $H_2O$  with an active site on the solid to give an adsorbed atom of oxygen, and the subsequent evaporation of CO from this site must preserve or replace the active site somehow. Thus when one active site reacts, another is regenerated in its place, so that the number of active sites remains virtually the same as reaction proceeds.

This picture is a reasonable one. A reactive site probably involves an atom on an edge or a corner having one or more high energy bonds (12); when this atom is removed one of its neighbors would very likely be left similarly situated.

Studies of electron spin resonance have shown that carbons which have been heated to over  $800^\circ C$  have very few unpaired electrons (at room temperature) so that the active site is probably not a surface free radical. Harker and co-workers (13) believe that in impure carbons, surface sites involving hydrogen or metallic impurities contribute more to the reactivity than do unpaired electrons. Perhaps the hydrogen and metal contents are sufficiently stable in carbon at  $900^\circ C$  after treatment at  $1000^\circ$  or  $1100^\circ$  so

that the number of atoms of each remains constant during a large part of the reaction. It seems unlikely, however, that the hydrogen content would remain so precisely constant during oxidation by  $\text{CO}_2$ , so a constant level of catalytic metallic impurities during the reaction appears to be a possibility for explaining the constant rates. This explanation would demand that a "stable" active site be associated or coupled with such an impurity, and it is certainly reasonable that a carbon atom on the edge of a graphitic crystallite might exchange electrons with a metallic atom contacting the same crystallite.

#### D. Effect of Thermal Treatment

Amorphous carbons usually (but not always) become less reactive upon heat treatment. The loss in reactivity with heat treatment shown in Figure 7 is therefore to be expected. The fact that reactivity plotted vs. time of heat treatment gives very roughly a straight line on log log coordinates as in Figure 7, shows that heat treatment decreases the reactivity quite rapidly at first and very much more slowly as the time of treatment is extended. The thermal soaking would be expected to permit local rearrangements or recrystallization of the carbon to anneal points of strain or perhaps to allow edge carbon atoms to orient themselves into a graphitic structure. Less reactive sites or perhaps isolated dislocations could be expected to stabilize themselves more slowly. At  $1000^\circ$  or  $1100^\circ\text{C}$  graphitization of an amorphous carbon hardly proceeds at all, and x-ray diffraction patterns of some of these heat treated carbons did not differ significantly from those of the "unsoaked" coke. Thus, while no gross recrystallization occurred in these heat treatments, it is logical to expect that very local rearrangements may have stabilized the carbon.

Figure 5 shows that the rate of reaction of the untreated or unheated Elkol coke falls off within  $2\frac{1}{2}$  hours to about the same rate as coke which had been heat treated at  $1000^\circ$  for seven hours. This decrease in rate of the untreated sample is too much to explain by the effect of the thermal treatment alone. Neither will reaction of binder carbon in the briquetted coke at a faster rate than carbon from the particles explain this decrease, since the calcined coal particles follow practically the same reaction paths as the coke. (See Table III.)

If active sites are regenerated during reaction they must migrate around the surface of the carbon so that occasionally an adjacent carbon atom might already be active and therefore both active sites might not be regenerated on reaction. However, while this factor could very well be appreciable in the later stages of reaction it apparently is not of importance in the heat treated samples and therefore it is hard to see why it might be significant in the untreated cases.

One possible explanation for the decrease in rate with unstabilized carbon could be that there are several types of reactive sites, some of which are much less stable and more reactive than others. This concept actually is highly likely and has often been cited. These more reactive sites would be those more readily annealed by the heat treating process and if they are not always regenerated on reaction but instead are replaced by less active sites, the rapid loss in reactivity of the untreated sample could be explained. Thus the heat treated samples would probably contain not only fewer reactive sites but also sites which are of a lower and more uniform order of reactivity and which are apparently regenerated in kind by gasification.

As another possibility, stable sites might be those associated with metallic impurities, while less stable, non-regenerated sites might be those solid defects that are readily healed by annealing.

#### VI. Summary

The principal finding of this work is that a carbon stabilized by suitable thermal treatment reacts with carbon dioxide at very nearly a constant rate during the consump-

tion of a major portion of the sample. This occurs under conditions where the overall rate of reaction is largely governed by the chemical step.

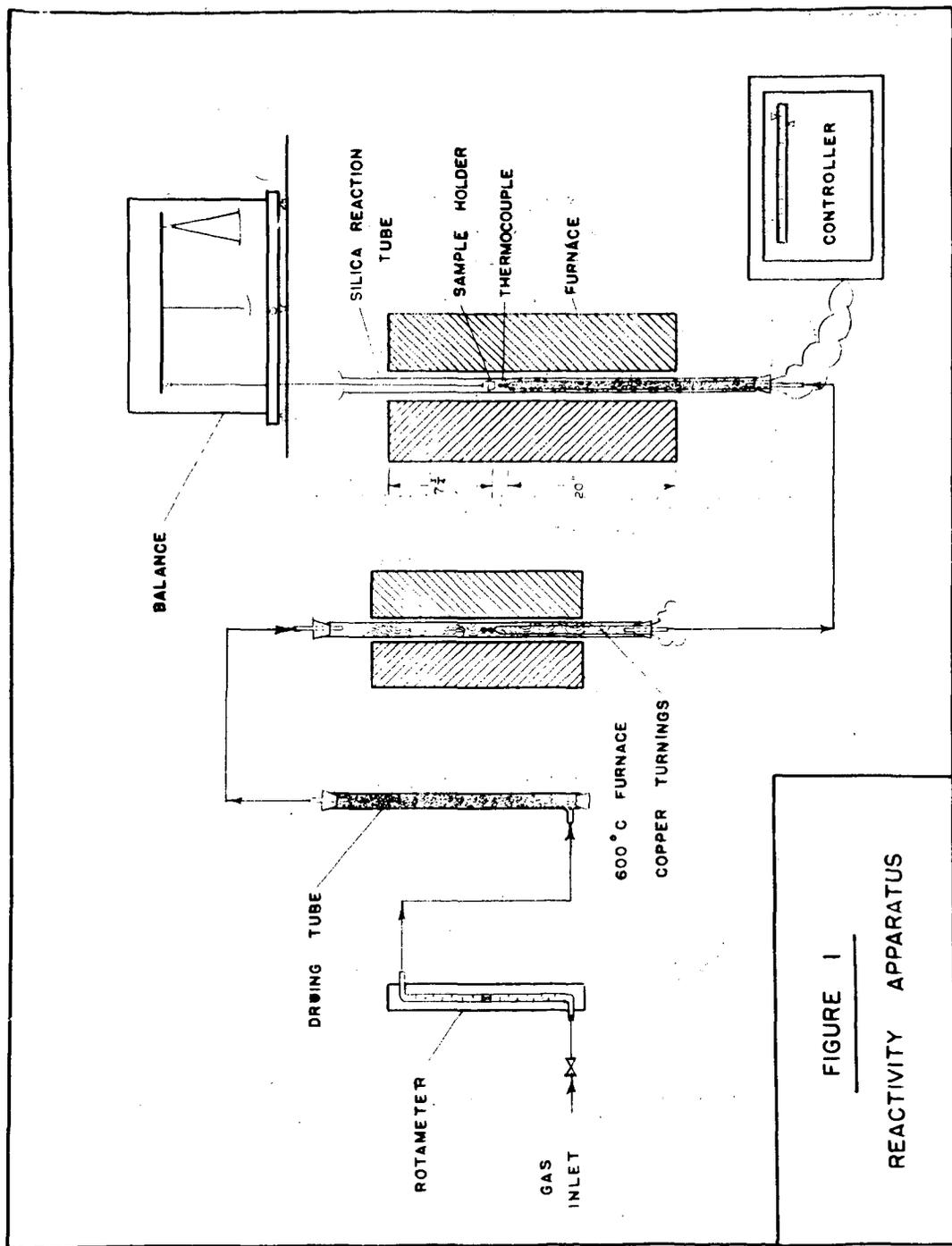
This constant reaction rate strongly suggests that every time a reactive atom of carbon leaves the solid state as carbon monoxide, another carbon atom is made reactive. Thus, during the course of oxidation the chemical state of the carbon surface remains constant even though the physical state (shape and surface area) changes.

With the unstable carbons the reaction rate falls off faster during reaction than during heat treatment alone. Therefore the chemical state of these carbons must change during the course of reaction. A possible hypothesis suggests that when a highly reactive site is removed from the solid matrix, it leaves behind a less reactive site so that the carbon stabilizes as reaction proceeds.

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**FIGURE 1**  
**REACTIVITY APPARATUS**

### REACTION OF HEAT-TREATED HELPER COKE

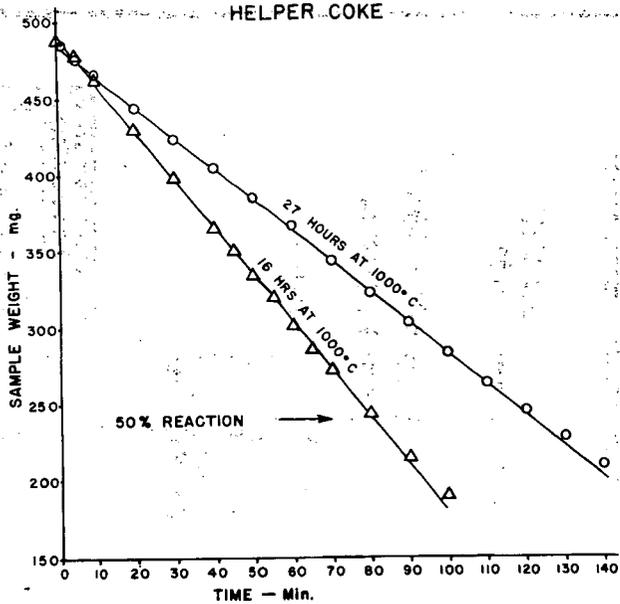


FIG. 2

### REACTION OF HELPER COKE SOAKED AT 1000° C

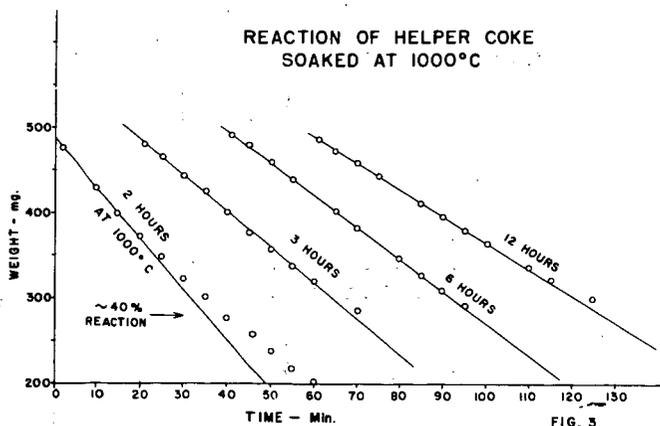
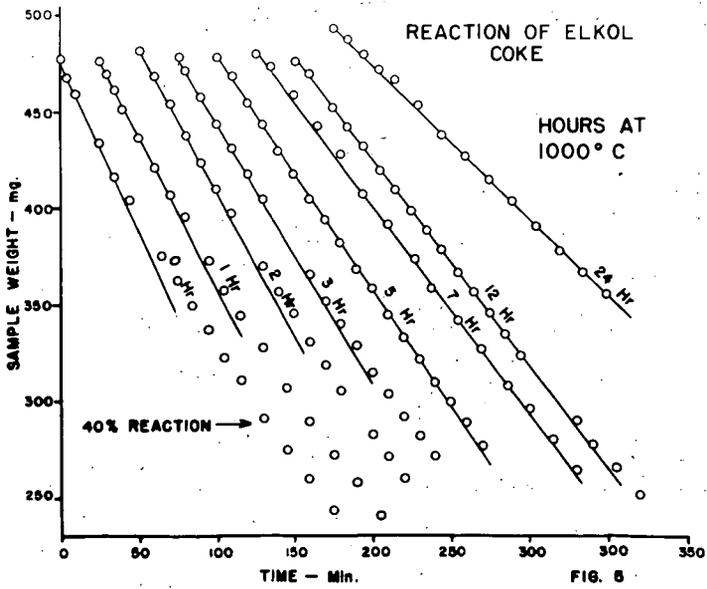
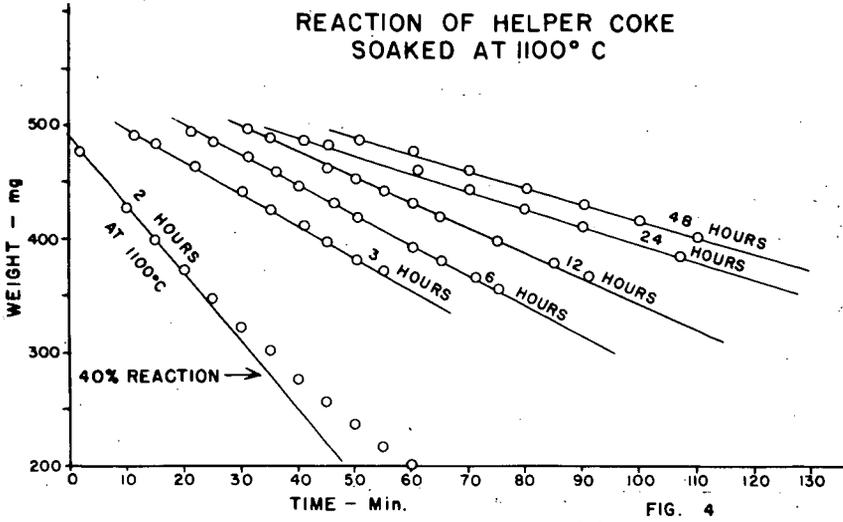


FIG. 3



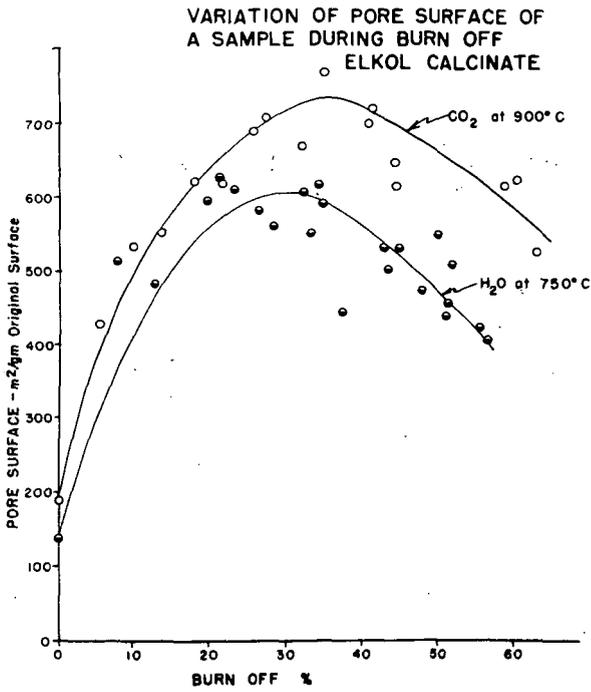


FIG. 6

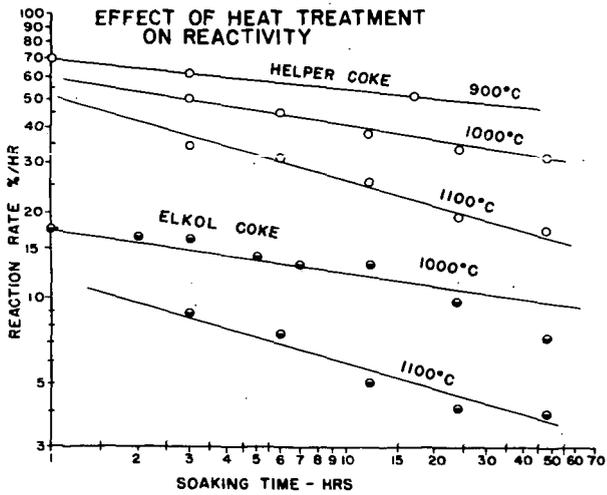


FIG. 7