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SURFACE STUDIES OF IRRADIATED GRAPHITE

By

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SURFACE STUDIES OF IRRADIATED GRAPHITE

INTRODUCTION

The nature of the microstructure of a solid can be determined by the use of certain surface study techniques. Properties associated with the microstructure of any porous solid are physical surface area and pore size distribution as well as some thermodynamic quantities. These are properties having a direct influence on solid-gas reaction kinetics. A complete study of graphite surface characteristics is probably necessary to understand the kinetics of chemical reaction between oxidizing gases and graphite. One of the primary objectives of surface studies work is to provide the type of information which is essential in these kinetics studies.

It is the purpose of this report to present the information obtained to this time concerning the change of graphite surface characteristics caused by various processes of oxidation and irradiation.

SUMMARY

Information is presented to aid the basic understanding of the kinetics of radiation-induced graphite-gas reactions. The apparatus used for this program has been described in detail in a previous report. (4)

Results developed in this report are:

1. The surface area of all graphite samples increases rapidly on slight oxidation. This increase is independent of size, type or form of graphite. For a slight amount of in-pile oxidation, the surface area of previously irradiated graphite samples increases more rapidly than that of equivalent virgin samples.
2. The surface area of graphite decreases upon exposure to low temperature irradiation; i. e., temperature of irradiation about 20 C to 50 C. This decrease is independent of the surrounding atmosphere in which the graphite is exposed.

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3. Oxidation opens up the larger of the closed graphite pores as well as the smaller ones with 20-35 Å pore radius. This process takes place in various stages during oxidation.
4. Low temperature irradiation causes a "shrinkage" or decrease in porosity for all sizes of radii on the surface of graphite.
5. The surface area of an irradiated graphite sample increases when thermally annealed and approaches asymptotically the surface area value obtained for the same sample before irradiation.

## RESULTS

There is evidence<sup>(1, 2, 3)</sup> to indicate that the study of changes in surface characteristics of pile graphite occurring during oxidation, irradiation, or both will enable one to explain an important portion of the kinetics of graphite-gas reactions. In order to study these changes of surface characteristics, a systematic series of experiments has been performed and the results found are presented in the first portion of this paper.

The experimental methods and the apparatus used for studies of the surface characteristics of graphite have been described in detail in a previous report.<sup>(4)</sup>

### Effects of Oxidation on the Surface Area of Graphite

Surface studies of graphite samples oxidized in an oven and in a Hanford pile reveal that the surface area increases for both samples during oxidation. However, in the case of samples oxidized in the pile, the increase in area is considerably greater than that for oven-oxidized samples. This holds true for samples oxidized to approximately the same extent.

Several virgin and irradiated samples of pile graphite were oxidized to various degrees and their surface areas determined. The extent

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of oxidation was measured by weight loss. Table I illustrates the effects of in-pile and oven oxidation on the surface area of several typical KC graphite samples.

Samples #87-139, #87-257, and #87-252 were cut from the same bar. The irradiated samples have a total exposure of 444 MD/CT. All samples listed in Table I were investigated as formed graphite. Surface area is calculated from the analysis of nitrogen gas absorption isotherms determined at liquid nitrogen temperature using the B. E. T. method.<sup>(5)</sup>

In Figure 1, the surface area in square meters per gram is plotted against the percentage weight loss due to oxidation for all samples in Table I. It is of considerable importance to note that there is a sharp increase of surface area on slight oxidation for all the samples listed in Table I. This increase, however, is considerably greater in the case of the irradiated samples.

Upon oxidation, the surface areas of other types of graphite increase in a manner similar to that of KC graphite. L. E. J. Roberts<sup>(6)</sup> and his co-workers have independently obtained identical results of surface area increase for oven oxidation of graphite. They have used thin plates as well as graphite powder samples for their experiments.

#### Effects of Radiation on the Surface Area of Graphite

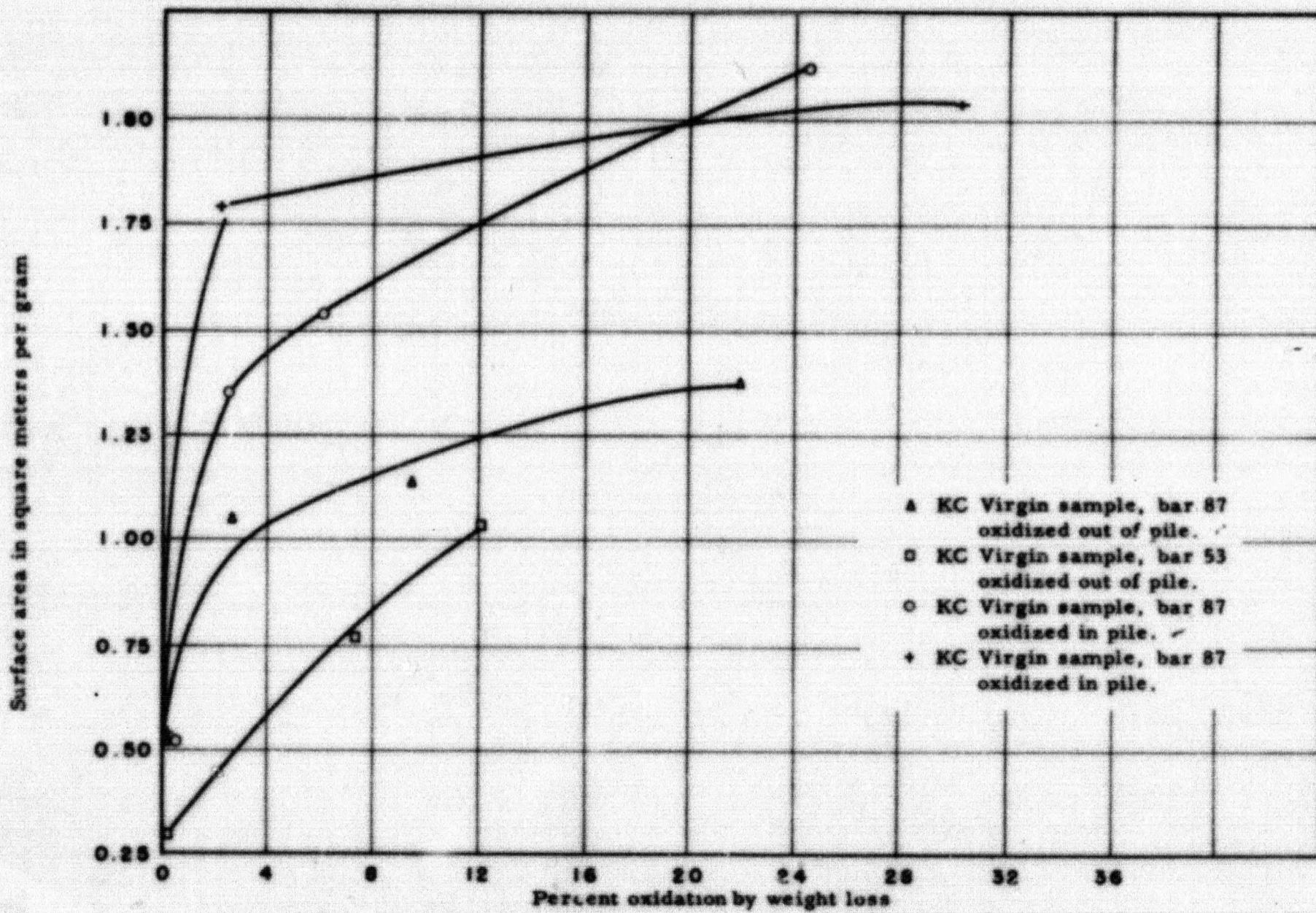
The changes of surface area with irradiation have been determined for various samples of graphites. It was found that in general the surface area of graphite decreases upon exposure to radiation at low temperatures.

For this experiment, a large number of graphite samples was exposed to radiation under different flux and atmosphere conditions but at low temperatures. The surface areas of these samples have been determined and the results are tabulated in Table II. The samples were all outgassed for three hours. The samples exposed in various atmospheres were enclosed into quartz containers in a manner described in detail elsewhere.<sup>(4)</sup>

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**TABLE I**  
**SURFACE AREA OF OXIDIZED GRAPHITE**

<u>Type and Sample No.</u>	<u>Per Cent Oxidation</u>	<u>Temperatures of Oxidation</u>	<u>Outgassing Temperature</u>	<u>Total Exposure MD/CT</u>	<u>Final Surface Area</u>
87-139 KC (Virgin)	0	---	450	0	0.52
" "	2.6	550	430	0	1.05
" "	9.6	600	350	0	1.13
" "	22.0	525	450	0	1.38
53-32 KC (Virgin)	0	---	450	0	0.30
" "	7.3	550	550	0	0.77
" "	11.9	660	350	0	1.04
87-252 KC (Virgin)	0	---	450	0	0.52
87-252 KC (Irradiated)	2.1	410	300 and 500	444	1.78
" " "	30.3	660	450	0	1.83
87-257 KC (Virgin)	0	---	450	0	0.52
" " (Irradiated)	2.4	410	450	444	1.35
" " "	6.0	525	350	0	1.53
" " "	24.5	525	450	0	1.92



CHANGE IN SURFACE AREA WITH INCREASING DEGREE OF OXIDATION  
FIGURE 1

**TABLE II**  
**EFFECT OF RADIATION ON THE SURFACE AREA OF GRAPHITE**  
**Test-Hole Irradiation at 50°C**

Sample and Type (#)	Exposure (MD/CT)	Before Irradiation		After Irradiation	
		Outgassing(4) Temperature (°C)	Surface Area (m <sup>2</sup> /gm)	Annealing Temperature (°C)	Surface Area (m <sup>2</sup> /gm)
--87-90, KC (Cylindrical Form, exposed in vacuum)	480	1000	0.52	350	0.47
				450	0.49
				550	0.49
--102-221, WSF (Powder, exposed in vacuum)	480	1000	3.98	300	3.50
				420	3.87
				650	3.96

**PROCESS TUBE WATER COOLED IRRADIATION AT 20°C**

Sample and Type (#)	Exposure (MD/AT)	Before Irradiation		After Irradiation	
		Outgassing(4) Temperature (°C)	Surface Area (m <sup>2</sup> /gm)	Annealing Temperature (°C)	Surface Area (m <sup>2</sup> /gm)
90-85, CSF (Powder, exposed in vacuum)	272	1000	6.20	75	5.35
				145	5.10
				165	5.18
				300	5.51
				500	6.02
80-104 (lampblack, Powder, exposed in vacuum)	272	1000	14.44	550	6.06
				70	11.97
				160	12.67
				300	13.08
				520	13.62
87-92, KC (Powder exposed in O <sub>2</sub> )	272	900	6.01	660	13.62
				75	13.62
				65	3.56
				125	3.66
				350	4.44
				550	4.58
630	4.69				
	650	4.84			
	720	4.84			

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**TABLE II (contd. )**  
**Process Tube Water Cooled Irradiation at 20°C**

Sample and Type (#)	Exposure (MD/AT)	Before Irradiation		After Irradiation	
		Outgassing(4) Temperature (°C)	Surface Area (m <sup>2</sup> /gm)	Annealing Temperature (°C)	Surface Area (m <sup>2</sup> /gm)
87-88 KC (Cylindrical Form Exposed in CO)	272	950	0.60	85	0.42
				150	0.43
				300	0.43
				450	0.44
				450	0.44
64-22 WSF, (Cut into three cylindri- cal pieces, exposed in CO <sub>2</sub> )	106	1000	0.95	400	0.66
				510	0.67
64-78 WSF, (Cut into two cylindrical pieces, exposed in CO <sub>2</sub> )	273	600	0.95	280	0.82
				450	0.85
				500	0.85
64-13 WSF, (Powder exposed in vacuum)	106	450	7.04	250	5.66
				400	6.16
				50	6.17

It is observed from the data in Table II that the surface area of all samples has decreased during irradiation. One also observes that the area of the irradiated samples increases with increasing outgassing temperature, but it never reaches the surface area value of the sample recorded before irradiation. Furthermore, the samples which initially have large surface area have shown the greatest decrease as compared to their corresponding virgin values.

In a previous report<sup>(4)</sup> it was mentioned that there was an indication that the surface area of pile graphite increases with exposure to irradiation. However, whether this increase was due to neutron flux or whether it was partially or wholly due to the reactions with the surrounding atmosphere had not been completely determined. This uncertainty has been

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clarified in the light of the information presented in Table II and discussed above, where both the previous history and the conditions of irradiation are known.

#### Effects of Oxidation on the Pore Size Distribution of Graphite

Pore size distribution studies on oxidized graphite samples indicate that oxidation opens up the larger of the closed pores as well as the smaller ones with 20-35 Å pore radius. This process takes place in a definite sequence of events during oxidation.

Graphite samples have been subjected to various degrees of oxidation and irradiation. The results are shown in Figures 2 and 3. The sequences of exposures portrayed in Figure 2 are:

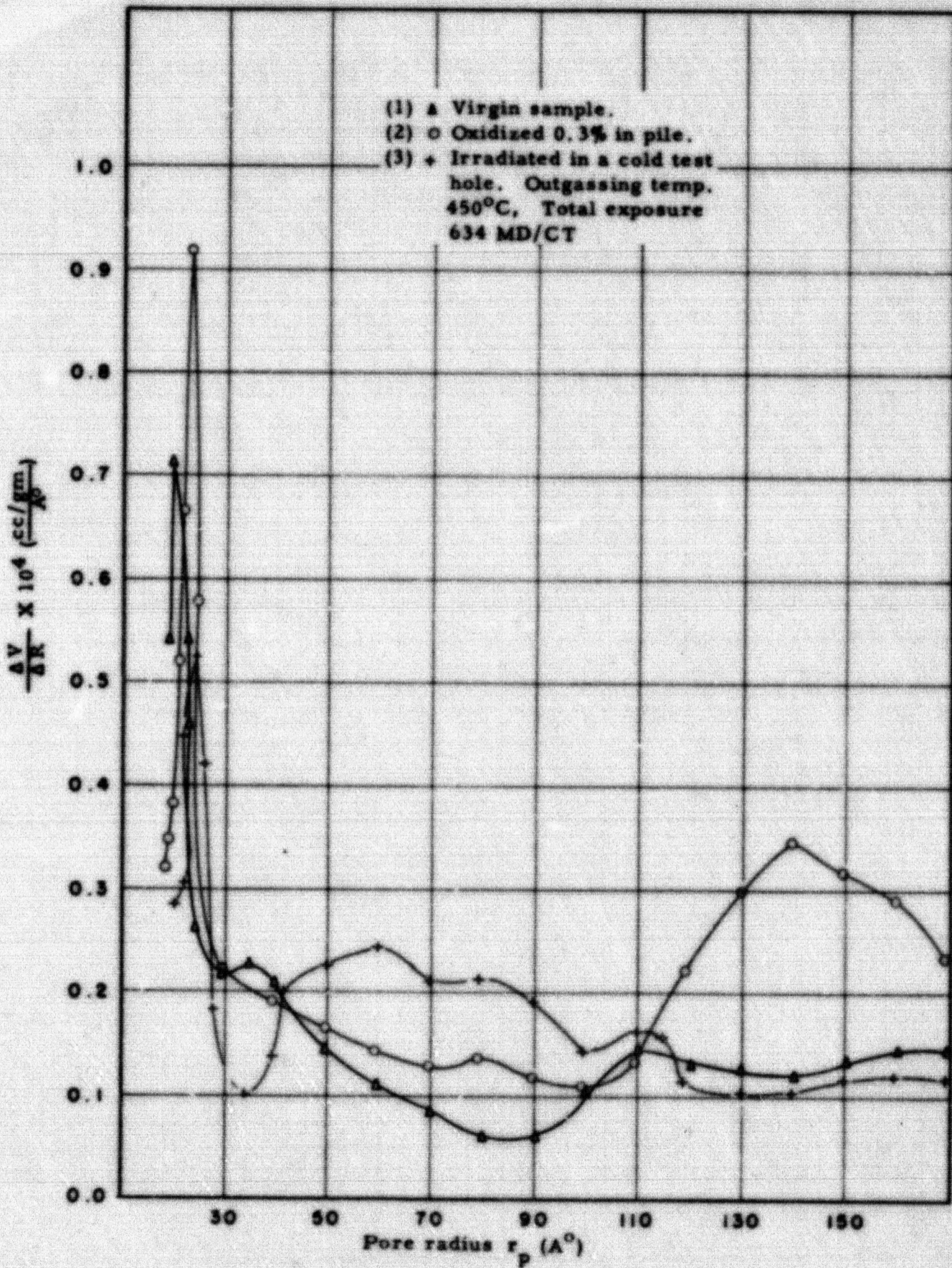
1. Oxidation of a sample in the pile to 0.3 per cent.
2. Irradiation of that sample in a cold test hole.

On the other hand, the sequences of exposure in Figure 3 are:

1. Oxidation of a sample, 2.4 per cent in pile. <sup>(4)</sup>
2. Oxidation of that sample about 6 per cent in oven.
3. Oxidation of the same sample about 30 per cent in an oven.

From reference to these figures, it is apparent that the principal peak of 20-35 Å pore radius present in all types of graphite investigated so far has changed in intensity with increasing degrees of oxidation. At first, with only a small percentage of oxidation this peak has increased in intensity. This is interpreted to mean that, with a small amount of oxidation, more pores of the 20-35 Å size radius have emerged. <sup>(4, 7)</sup> As the oxidation proceeds, however, the number of small pores decreases as can be seen in Figure 3, where the oxidation is six per cent. Between six and thirty per cent oxidation this principal peak changes very little. On the other hand, the peak at 90-150 Å increases in intensity up to about six per cent oxidation <sup>(6)</sup> and then decreases for thirty per cent oxidation.

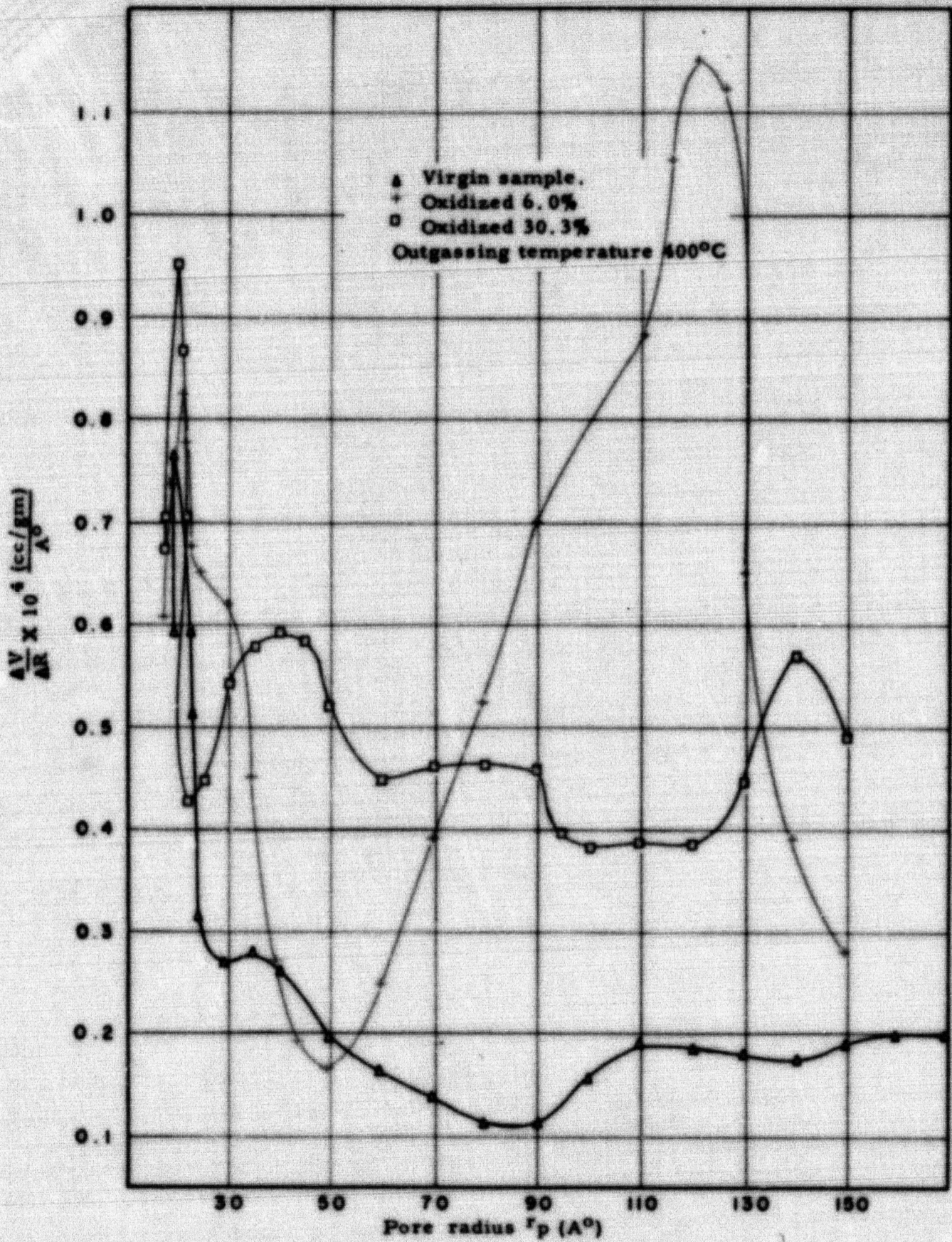
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PORE SIZE DISTRIBUTION CURVES FOR  
GRAPHITE SAMPLE # 87-232 KC

FIGURE 2

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PORE SIZE DISTRIBUTION CHANGE WITH OVEN OXIDATION FOR GRAPHITE SAMPLE # 67-252 KC

FIGURE 3

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The samples used for the study of pore size distribution versus oxidation were investigated both as formed as well as powdered graphite. A total of seven samples of KC and CSF type of artificial pile graphites were investigated, and the results agree well with one another within the experimental error. The total area in square meters per gram found by summing the areas in the pores and the area computed using the B. E. T. (5) method agree very well for all runs. The construction of the pore size distribution curves is derived from the nitrogen desorption isotherms on graphite at liquid nitrogen temperatures, using the B. J. H. method. The assumptions, validity and applicability of this method have been discussed previously elsewhere. (4, 9)

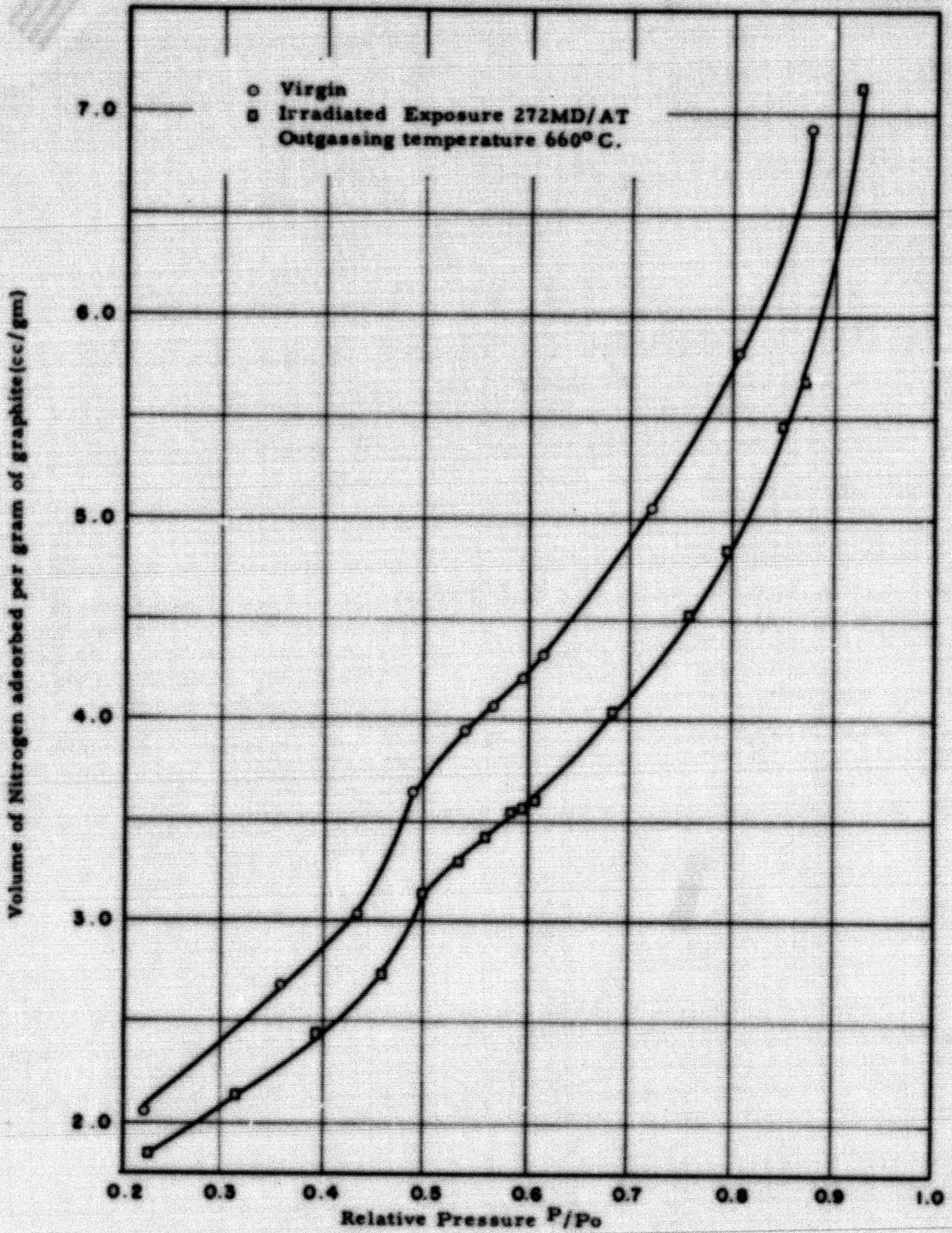
#### Effects of Radiation on the Pore Size Distribution of Graphite

Several experimental runs with various virgin and irradiated graphite samples reveal some important changes of their pore size distribution due to radiation. In general, samples having a large surface area were affected relatively more by pile irradiation than were those having small surface area.

Typical nitrogen gas desorption isotherms of graphite before and after irradiation are presented in Figures 4 and 5 for convenient comparison.

The pore size distribution curves derived from these isotherms and illustrated in Figures 6 and 7 clearly indicate the effect of radiation damage on the pore size of a given graphite sample. In Figures 6 and 7, a general "shrinkage" or decrease in porosity is observed for all sizes of pore radii. This phenomenon is typical of all samples studied so far. The irradiation for the samples investigated took place in a water-cooled process tube (annulus tube) in a Hanford pile with an average temperature of about 20 C. The samples, both in formed as well as powdered state, were enclosed in quartz tubes, outgassed to 660 C and evacuated to  $10^{-6}$  mm Hg for several hours before sealing. Several of the quartz containers

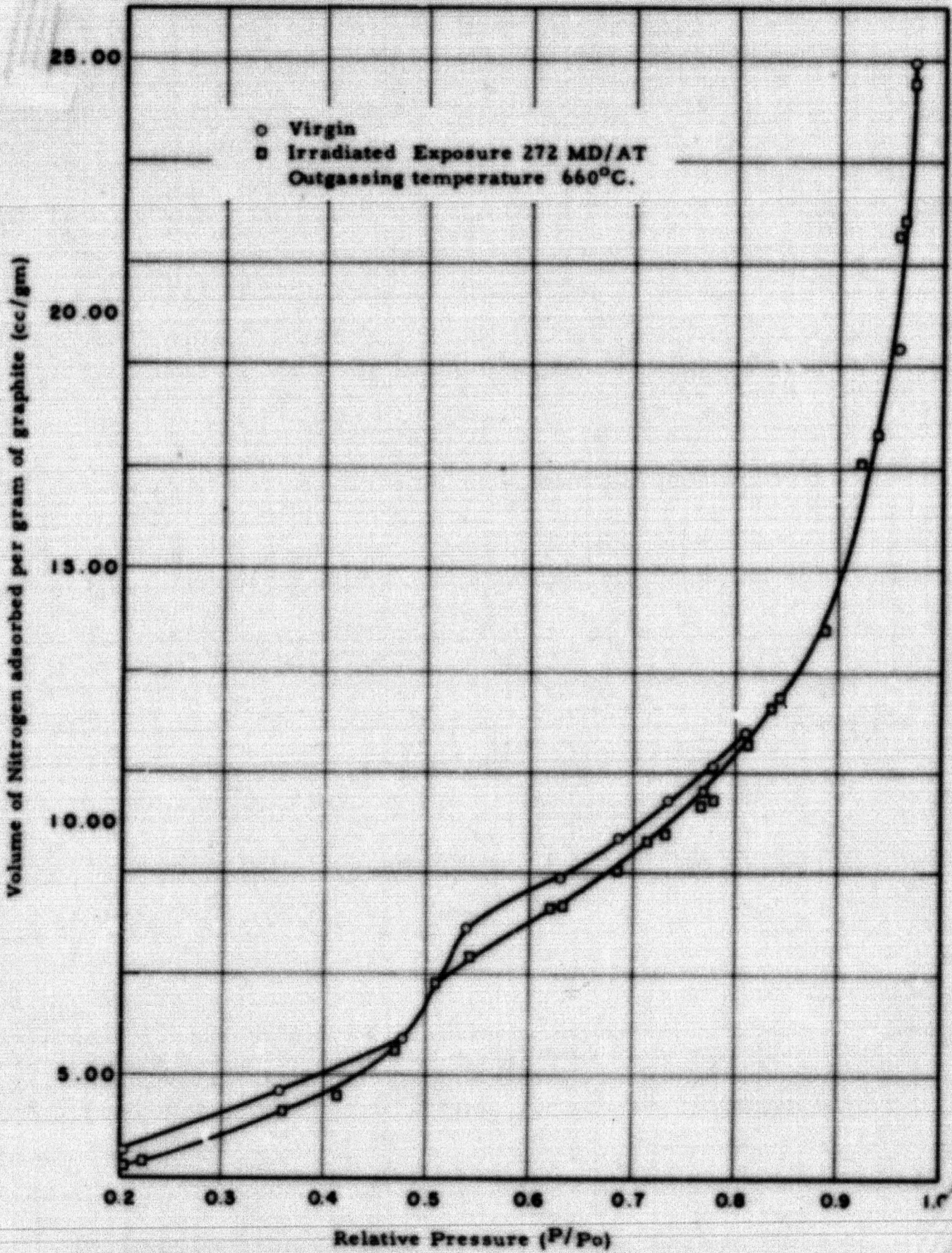
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DESORPTION ISOTHERMS FOR A TYPICAL KC GRAPHITE, POWDERED  
SAMPLE IRRADIATED IN OXYGEN AT  $\sim 20^\circ\text{C}$ . SAMPLE # 87-92

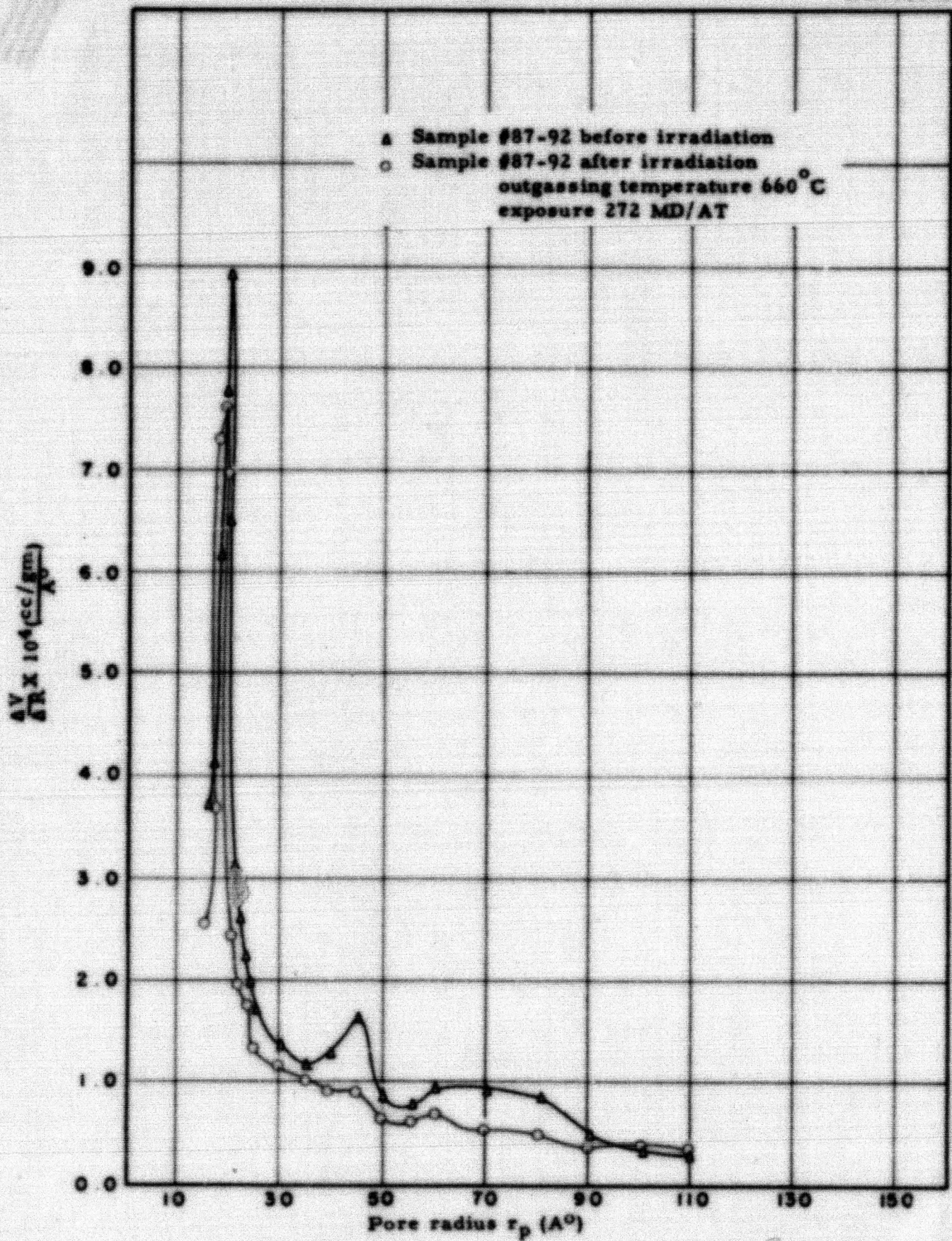
FIGURE 4

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DESORPTION ISOTHERMS FOR A TYPICAL TS GRAPHITE, POWDERED  
SAMPLE IRRADIATED IN VACUUM AT ~ 20°C. SAMPLE # L-19-2 TS  
FIGURE 5

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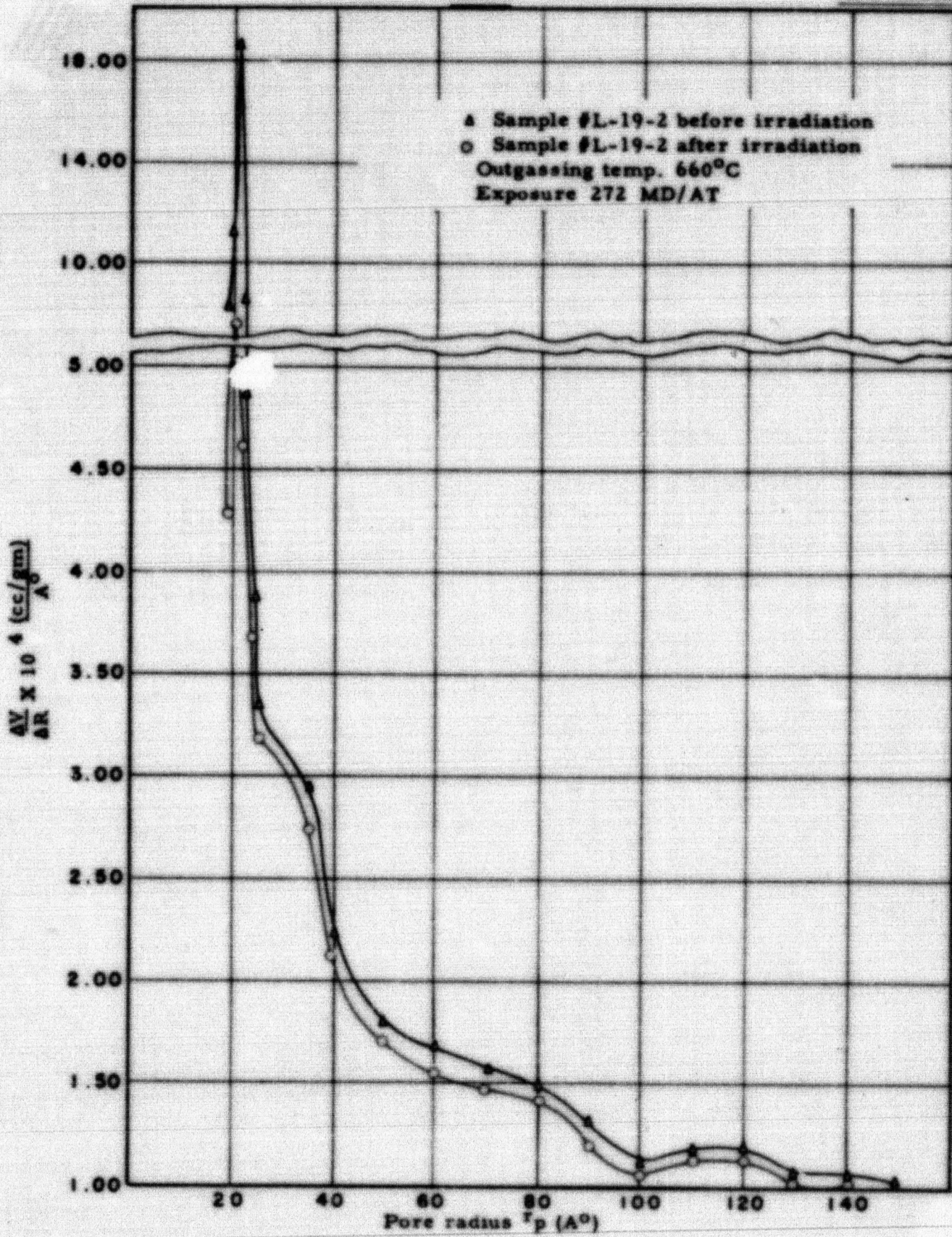


PORE SIZE DISTRIBUTION CURVES FOR A TYPICAL KC GRAPHITE SAMPLE IRRADIATED IN OXYGEN AT  $-20^\circ \text{C}$

FIGURE 6

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PORE SIZE DISTRIBUTION CURVES FOR A TYPICAL T S GRAPHITE SAMPLE IRRADIATED IN VACUUM AT ~20 ° C

FIGURE 7

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in addition to graphite samples were filled with various gases after evacuation.<sup>(10)</sup> Up to the present, however, only the samples exposed in oxygen and vacuum have been studied. As it is observed from the curves in Figures 6 and 7, there is no great difference of damage between the two samples exposed in oxygen and vacuum respectively. The quartz containers of most of the samples were found in excellent condition after exposure to radiation. All of these containers were leak-tested with a manometer before and after the break-off seal was opened.

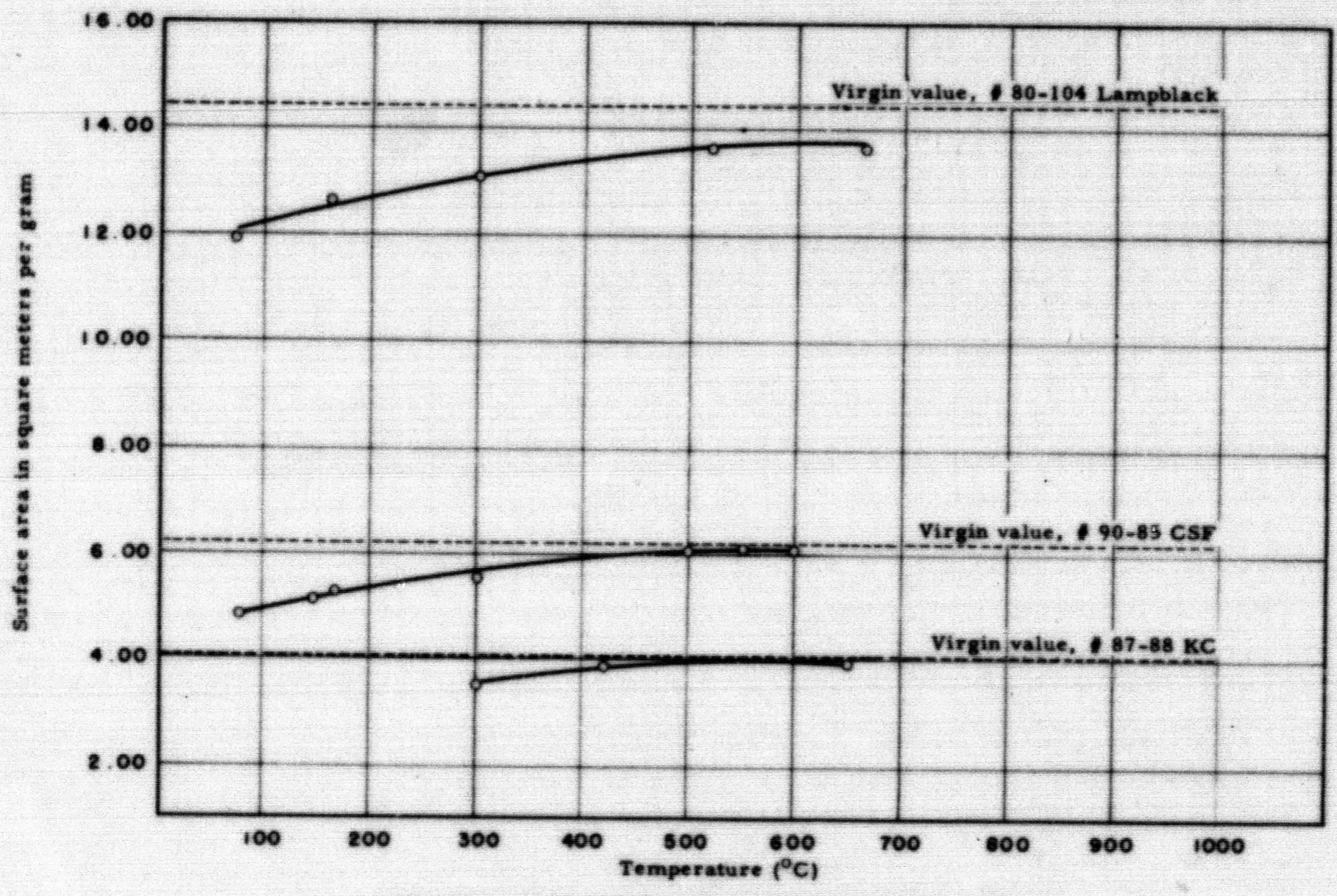
#### Temperature Annealing Effect on the Surface Area of Irradiated Graphite

The surface area of pile graphite decreases with low temperature irradiation. It is, however, of importance to note in Table II that the surface area having been reduced by irradiation will increase on thermal annealing treatment. In addition, one observes that, although the area increases with increasing annealing temperature, it approaches asymptotically the value measured for that sample before irradiation. It was first thought that this area variation was just a normal increase with increasing outgassing temperature, as in the case of virgin samples.<sup>(11)</sup> This has been proven not to be the case. A sample, #80-10<sup>4</sup> was first outgassed to 660 C and its surface area determined. Then, a . was allowed to enter the sample container and remain in it for about an hour or two. The sample was then outgassed at 75 C for three hours and the surface area determined. There was no difference in sample area values between the two runs.<sup>(12)</sup> This procedure was repeated with many other samples, with similar results. It was therefore proven conclusively that the surface area increase of the irradiated graphite samples was due to temperature annealing. The temperature annealing effect is illustrated in Figure 8.

#### DISCUSSION OF RESULTS

The experimental results obtained from studies of the surface characteristics of irradiated graphite were described in the preceding sections. In the following section, the meaning of these experimental results will be discussed in more detail.

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TEMPERATURE ANNEALING EFFECT ON THE SURFACE AREA OF VACUUM IRRADIATED GRAPHITE

FIGURE 8

Variation of Pore Size Distribution and Surface Area of Graphite Due to Oxidation

For all types of artificial graphite investigated, the surface area increases with increasing degree of oxidation. The surface area increases rapidly on slight oxidation, the amount of the increase being independent of the size of the specimen or of whether it is formed or powdered graphite. The oxidation effect on the surface area is illustrated in Figure 1. With the same degree of oxidation concurrent with irradiation, the irradiated graphite samples show a far greater increase in surface area than the non-irradiated samples. The meaning of surface area increase with increasing degree of oxidation has been discussed previously.<sup>(4)</sup>

Pore size distribution studies indicate that oxidation opens up the larger of the closed pores as well as the smaller ones at 20-35 Å radius. This is interpreted to mean that some pores are not accessible to the nitrogen used to measure surface area. Before oxidation, crystalline or semi-crystalline aggregates block the larger pore entrances. Some pore blockages are then removed by oxidation. These "blockages" may be poorly crystallized material lying between well formed crystallites, binding material used in the manufacture of graphite or both. In the case of irradiated graphite, the possibility exists that activated regions or crystallite distortions can be produced by neutron flux, which will make oxidation comparatively easier than the undamaged bulk of the graphite.

The interpretations outlined above are further substantiated by the results obtained from the study of pore size distribution of oxidized graphite. The study of change in pore size distribution with varying degrees of oxidation has yielded information which may be interpreted in terms of a sequence of oxidation events.

In graphite, two of the principal distribution peaks in the micropore structure occur at about 20-35 Å radius and 90-150 Å radius. With increasing oxidation, the peak intensity at 20-35 Å rises rapidly between zero and

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about two per cent oxidation. It decreases in intensity between two and six per cent oxidation and changes very little between six and thirty per cent. On the other hand, the peak at 90-150 Å increases in intensity up to about six per cent oxidation.

These changes can be interpreted to mean that the following sequence of events takes place:

1. Between zero and two per cent oxidation some type of material is removed which had previously blocked access to some 20-35 Å pores. This occurs in the region of the rapid increase of surface area with slight oxidation. It can be termed "easily oxidizable matter."
2. Between two and six per cent oxidation, the smaller pores are opened to produce larger pores until the blocking material is removed. At this point the rate of increase of surface area with increasing degree of oxidation diminishes as is shown in Figure 1.
3. Beginning at an oxidation somewhat greater than six per cent, apparently some process is occurring which does not greatly effect the pore size distribution. This could be generalized oxidation of graphite crystals.

These surface changes can be compared with the chemical reaction rates. Studies of rate reactions of graphite oxidized in a tube with carbon dioxide gas at 1000 C indicate a rapid initial rise in reaction rate to a value of 0.10 gm/gm sample per day at two per cent oxidation. At this point, the reaction rate remains constant until about seven per cent of the sample has been oxidized. (13) From about seven to sixteen per cent oxidation the reactions rate increases linearly but at a much slower rate than before. One observes that the sharp increase of burnout rate corresponds to a sharp increase of surface area on slight oxidation. Furthermore, the linear oxidation rate increase above seven per cent corresponds to slow

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increase in surface area and very little change in the pore size distribution. This latter portion of the burnout rate may be due to oxidation of perfect graphite particles. Additional experimental work is now being carried out in an attempt to correlate the rate of oxidation with the surface characteristics of graphite.

Variation of Pore Size Distribution and Surface Area of Graphite Due to Radiation

For all types of pile graphite investigated, the surface area decreases with low temperature irradiation. This is true for samples irradiated in vacuum as well as for those irradiated in various atmospheres.

Investigation of pore size distribution curves for low temperature irradiated samples shows a general "shrinkage" or decrease in porosity for all sizes of pore radii.

If samples irradiated at low temperatures are heated at relatively high temperatures the surface area increases very gradually and slowly approaches the area value found before irradiation for each respective sample. This annealing effect is shown in Figure 8.

The decrease in surface area and general lowering of intensity for pore size distribution peaks of irradiated graphite can be attributed to physical expansion of the individual crystallites. These individual crystallites expand due to radiation flux and in doing so occupy the microscopic void spaces that are available in their immediate vicinity. This causes a decrease in porosity. Many pores, however, are known to be very small in size, or they may be large but have small "bottle neck"-like openings. (5,14) These small pores are partially or completely blocked due to graphite crystalline expansion, thus causing a decrease in available surface area.

Subsequent thermal annealing results in a decrease of physical expansion forcing the crystallites back to their original positions and thus making the original surface available.

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Further experimental work is in progress to consolidate the results found on surface characteristics due to low temperature irradiation. These results will be of importance in helping to explain the gas-graphite reaction kinetics as well as the radiation-induced reactions between graphite and surrounding atmosphere in the Hanford piles.

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ABSTRACT

The effects of oxidation and irradiation on the microsurface structure of pile graphite have been investigated by measuring the surface area and pore size distribution of several samples. The results obtained for both oxidized and irradiated graphite samples indicate that changes in surface characteristics which occur are determined by the flux, temperature of irradiation, and gaseous atmosphere in which the radiation takes place.

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