HW-68493

UC-4, Chemistry
(TID-4500, 16th Ed.)

OXIDATION OF GRAPHITE
UNDER HIGH TEMPERATURE REACTOR CONDITIONS

By

R. E. Dahl

Materials Development
Reactor and Fuels Research and Development
Hanford Laboratories Operation

July, 1961

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract No. AT(45-1)-1350 between the
Atomic Energy Commission and General Electric Company

Printed by/for the U. S. Atomic Energy Commission

Printed in USA. Price \$1.00. Available from the
Office of Technical Services
Department of Commerce
Washington 25, D.C.

This document is
PUBLICLY RELEASABLE
Barry Steele

Authorizing Official
Date: 6/4/64

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

A kinetic study was conducted to provide information on oxidation of reactor graphites in the temperature range 450-675 C and on the effects of reactor environment on oxidation rates. Among the parameters studied were chemical reactivity of the graphite, prior oxidation, a high intensity gamma flux during oxidation, variation of the surface-to-volume ratio of the graphite specimens, neutron bombardment prior to oxidation exposure, and gas flow rates. Rate equations showed apparent activation energies of 50 kcal/mole in the absence of radiation and 30 kcal/mole in the presence of a 1×10^6 r/hr gamma flux.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION.	4
SUMMARY	4
EXPERIMENTAL DETAILS	5
Apparatus	5
Samples	8
Procedure	9
KINETICS	9
OTHER VARIABLES WHICH INFLUENCE OXIDATION RATES	14
Chemical Reactivity	14
Effect of Prior Oxidation	16
Effect of Gamma Flux	17
Effect of Prior Neutron Irradiation of the Graphite	21
CONCLUSIONS	21
ACKNOWLEDGMENTS	22
APPENDIX I - DETERMINATION OF THE ACTIVE ZONE	25
APPENDIX II - ANALYSIS OF VARIANCE OF FACTORIAL EXPERIMENT DATA	27
REFERENCES	33

OXIDATION OF GRAPHITE
UNDER HIGH TEMPERATURE REACTOR CONDITIONS

INTRODUCTION

Oxidation of graphite in high-temperature, graphite moderated, gas-cooled reactors is important from two standpoints. First, oxidation by trace impurities in the coolant could weaken the moderator structure and reduce the life of the reactor. Second, rupture of a coolant line during operation could cause displacement of the coolant by air and extreme oxidation of the graphite. Under these circumstances, heat could be generated more rapidly by oxidation of the graphite that it could be removed. The resulting rise in temperature could cause a "runaway" oxidation situation and severely damage the reactor.

This report is mainly concerned with the definition of the variables which are important in runaway oxidation situations. Experiments were conducted to develop analytical methods of predicting graphite oxidation rates under conditions encountered in high-temperature gas-cooled reactors, particularly the Experimental Gas-Cooled Reactor (EGCR). The effects on oxidation of gamma flux, prior irradiation, prior oxidation, and impurities in the graphite were investigated.

SUMMARY

Over the temperature range 400 to 675 C and at one atmosphere pressure, graphite oxidation was observed to proceed as a near first-order reaction with respect to oxygen. The activation energy of the graphite tested is 50 ± 5 kcal/mole.

Up to 650 C, oxidation rates were increased by a gamma flux of 1×10^6 roentgens per hour (r/hr). Enhancement of the rate decreases with increasing temperature, since the observed activation energy in the gamma flux was about 20 kcal/mole less than that of thermal oxidation. At expected EGCR operating temperatures (~ 600 C), oxidation rates were increased a factor of three by gamma radiation.

Oxidation rates of preoxidized graphite exceed those of unoxidized graphite. As oxidation proceeds, rates generally increase over the first few per cent burnoff and then stabilize over a wide burn-off range.

Chemical reactivity was found to vary widely among reactor grade graphites, apparently as a function of the concentration of impurities. Less pure graphites tend to pit badly during oxidation while purer graphites undergo uniform surface oxidation.

Neutron bombardment of the graphite to an exposure of 4×10^{19} nvt ($E > 0.18$ Mev) at 550 C had no discernible influence on oxidation rates.

EXPERIMENTAL DETAILS

Apparatus

Oxidation rates were determined by following graphite weight loss at controlled temperatures and gas flows. Two sets of apparatus were employed, one for thermal experiments, Figure 1, and the other for experiments in a 10^6 r/hr gamma flux from a Co^{60} source, Figure 2. In each apparatus, the sample was positioned in a furnace and weighed periodically during the course of the reaction without disturbing the system.

The gas used in the experiments was predried through silica gel columns prior to entry into the test zone. Flow was 2.0 scfh in all experiments except those investigating the effect of flow rate, where rates of 0.2 and 5.0 scfh were also used. Air or oxygen at one atmosphere pressure was used in all experiments.

Temperature was controlled to ± 5 C with proportional off-on, or three-mode controllers. The hot junctions of actuating thermocouples were positioned within 1/16 inch of the lower end of the samples. Radiation shields were not used, since simultaneous readings from control thermocouples and thermocouples embedded in a sample showed no significant difference (< 2 C). Temperature profiles were made of the test zones in both sets of apparatus, and sample positions were chosen where a temperature gradient of less than 2 C existed over the two-inch sample length.

FIGURE 1

Graphite Weight Loss Equipment

FIGURE 2

Apparatus Used for Oxidation Experiments in a Gamma Flux

The temperature dependence of graphite oxidation necessitated careful cross calibration of temperature control between the thermal oxidation equipment and the gamma facility before rates could be compared. To accomplish this, the reference thermocouple used to calibrate the gamma facility was calibrated against the control thermocouple in the thermal apparatus between 400 and 700 C. A uniform difference of 15 C between the facilities was determined and rates were corrected accordingly.

Samples

Graphite samples were usually sleeves, 2 inches in length by 0.426-inch OD by 0.250-inch ID. To investigate the effect of a change in surface-to-volume ratio, some cylindrical samples 2 inches in length by 0.426-inch OD were used. The longitudinal axes of all samples were machined parallel to the extrusion axes of the whole bar of graphite in order to simulate the exposed surfaces in the EGCR which are also of parallel orientation.

There was no pretreatment of the samples prior to oxidation other than careful vacuuming of machining dust from the surface. All sample handling which occurred between machining and insertion in the reaction chamber was done with rubber-tipped forceps to prevent possible contamination of the surface with catalytic salts.

Purity of each full bar of graphite was determined prior to machining by measuring changes which it caused in reactivity of the Hanford Test Reactor. Reactivity changes are expressed as differential inhours (dih), which may be related to the absorption cross section expressed in millibarns by the formula⁽¹⁾

$$\sigma_a (2200 \text{ m/sec}) = (4.47 \pm 0.04) - (0.733 \text{ dih} \pm 0.03).$$

Purity values range from +1.10 to around +0.70 for gas-purified graphites and from +0.70 to 0.0 for most other reactor graphites. In some cases, graphites with values as low as -0.30 have been used in reactor applications.

It must be remembered that purity values determined in this manner depend upon the absorption cross section of the isotopes as well as their concentration. Thus, spectrographic analyses were also made for studies of chemical reactivity.

Procedure

Rate equations were determined by a series of weight loss experiments conducted at temperatures ranging from 450 C to 650 C and at one atmosphere pressure. Weight loss rates used in these determinations were steady-state rates, that is, calculated during a period of burnoff when the rate did not vary with time. Gas flow variation, prior irradiation of graphite, and sample geometry were examined as variables. Since four variables were involved, a factorial experiment was designed to determine most efficiently the effect of each variable. Sixteen weight loss experiments were conducted to fulfill a half replicate of a 4×2^3 design in which two levels of each of the three variables were studied at four temperature levels. Experimental design, data, and an analysis of variance performed on the data are presented in Appendix I.

KINETICS

Graphite oxidation under the conditions of this investigation is a complex reaction that may be controlled by one or more physical and chemical mechanisms. As stated by Walker, ⁽²⁾ the reaction between oxygen and graphite may be controlled by one or more of the steps which influence reactions between a gas and a porous solid.

1. Chemisorption of reactant, wholly or in part; rearrangement of chemisorbed species on the surface to desorbable products; desorption of products from the surface (Zone I reaction).
2. Diffusion of the reacting gas from the exterior surface to an active site beneath the surface, and of products in the opposite direction (Zone II reaction).
3. Mass transport of reacting gas and products across a relatively stagnant gas film between the exterior surface of the solid and the main gas stream (Zone III reaction).

A Zone I reaction is controlled by Step 1 and is marked by temperature dependence only; hence, the apparent activation energy is the true value. No reaction gradient would exist theoretically through the sample, since all active sites would be available to the reactant. The rate equations developed in this paper are valid only for a Zone I reaction, since only temperature dependence was considered in their derivation.

Variation of the surface-to-volume ratio would influence the reaction rate if the reactions were proceeding in Zone II. Experimentally, no difference in oxidation rates was noted when surface-to-volume ratio was varied from 20 cm^{-1} (sleeves) to 8 cm^{-1} (cylinders) as seen in Appendix I. In these two cases the fractions of the sample calculated to be reacting were 0.97 and 0.84, respectively (Appendix II). Further confirmation of the assumption that a Zone I reaction was observed is the fact that the activation energy for thermal experiments was constant over the temperature range investigated. Had the reaction shifted into Zone II or into an intermediate zone at higher temperatures, the activation energy would have been reduced from the true (lower temperature) value to approximately one half that value.

However, a note of caution should be interjected at this point. Although oxidation of the samples used in this investigation was not diffusion-controlled, this would not be true for large graphite blocks used in reactor application. In such case, it would be necessary to solve the diffusion equation for the particular geometry in question and determine the depth of the active reaction zone. This zone would contain the reacting mass of graphite to be considered in oxidation calculations. As an example, the active zone in the EGCR moderator at 600 C was calculated to be about 0.5 cm in depth.

The possibility that the reaction proceeded in Zone III was studied by varying the flow rate above that needed to provide a stoichiometric oxygen concentration. The flow was varied from 0.2 scfh to 2.0 scfh in the factorial experiment, and up to 5.0 scfh in other experiments in both the gamma irradiation and thermal facilities. There was no effect on the oxidation rates. A factor of three would have been noted had mass transport influenced the reaction, since Zone III reactions are marked by an approximate zero activation energy and a half-power dependence on flow rates.

Reactions studied may therefore be considered in Zone I and hence, dependent only upon the chemical reactivity of the graphite and on the temperature.

Analysis of experimental data for thermal oxidation of CSF graphite with both air and oxygen (Table I) yields the following rate equations for gasification of carbon.

$$r = 9.22 \times 10^8 e^{-45.2 \times 10^3/RT} \text{ (g/g-hr) air-graphite,}$$

and

$$r = 5.61 \times 10^{10} e^{-50.2 \times 10^3/RT} \text{ (g/g-hr) oxygen-graphite}$$

Analysis of variance of the data demonstrates an average experimental error of 50 per cent at the 95 per cent confidence level in the individual weight loss experiments.

The observed activation energies are 45.2 kcal/mole for air-graphite experiments and 50.2 kcal/mole for the oxygen-graphite. If all are considered to be the same reaction, oxygen-graphite, an activation energy of 48 ± 4 kcal/mole is determined, substantially agreeing with other investigations.^(2, 3) The Arrhenius plots of the data are shown in Figure 3.

The order of the observed reaction with respect to oxygen, n , may be calculated from the difference in the rates of the air-graphite and oxygen-graphite reactions. Applying the differential method of Vant Hoff⁽⁴⁾ which states

$$n = \frac{\log (dc_1/dt) - \log (dc_2/dt)}{\log c_1 - \log c_2}$$

and substituting data at 600 C,

$$n = 0.7 \pm 0.3.$$

Thus, the reaction is first or near-first order with respect to oxygen pressure, agreeing with other investigations^(5, 6) made under varied conditions. Disagreement is found only in observations^(7, 8) made at low pressure ($< 100 \mu\text{-Hg}$).

TABLE IOXIDATION RATES OF CSF GRAPHITE IN THE ABSENCE OF RADIATIONAir Oxidation (2.0 scfh)

<u>Temperature, C</u>	<u>Rate, (hr⁻¹) x 10³</u>
500	0.223
520	0.290
550	1.13
600	4.90, 4.15, 6.40
625	12.3
650	21.0
675	32.6, 38.1
700	108

Oxygen Oxidation (2.0 scfh)

450	0.0546
500	0.519
520	0.760
550	3.85, 2.35
575	8.10
600	15.8, 16.9, 24.1, 23.1
625	47.7, 28.1, 25.7
650	123, 110, 80.1
675	192

Least Squares Analysis:

$$\text{Assume } r = Ae^{-E/RT}$$

Limits are at one standard deviation.

Air-Graphite:

$$r = 9.22 \times 10^8 e^{-45.2 \times 10^3/RT} \text{ (hr}^{-1}\text{)} \pm 24 \text{ per cent}$$

Oxygen-Graphite:

$$r = 5.61 \times 10^{10} e^{-50.2 \times 10^3/RT} \text{ (hr}^{-1}\text{)} \pm 28 \text{ per cent.}$$

FIGURE 3

Arrhenius Plot of CSF Graphite Oxidation Data

OTHER VARIABLES WHICH INFLUENCE OXIDATION RATES

Chemical Reactivity

Chemical reactivity of graphite can be influenced by a number of factors, such as density, type of coke, type of binder, particle size, gas permeability or porosity, and particle orientation. On the basis of work done by Clark, ⁽⁹⁾ purity appeared to determine the reactivity to a much greater extent than any of the other variables within the range of permeabilities studied. The range of oxidation rates at 600 C for series of graphites, whose properties other than purity are nearly identical, may be seen in Table II. Since it may be reasonably assumed that the activation energy of each reaction is the same, frequency factors vary from 5×10^9 to 5×10^{11} .

TABLE II

OXIDATION RATE AS A FUNCTION OF PURITY AT 600 C

Air at 2.0 scfh

<u>Graphite Type</u>	<u>Rate, (hr⁻¹) x 10²</u>	<u>dih</u>
SP-21	2.52	+0.027
TS-AGOT	1.92	+0.180
SP-23	1.87	+0.317
CO	1.60	+0.360
SP-10	1.47	+0.671
EGCR	1.33	+0.71
CSF	0.52	+0.854
SP-7	0.429	+1.10

Purity appears to govern the manner in which oxidation attacks the graphite surface. That purified graphite is attacked uniformly over the surface while less pure graphites are badly pitted, indicates localized attack in the vicinity of high concentrations of impurities, as illustrated in Figure 4.

A. EGCR Graphite

B. CSF Graphite

FIGURE 4

Effect of Impurities Demonstrated by Appearance
of Sample after Exposure in Air at 600 C for 24 Hours

To assist in evaluation of runaway oxidation hazards, oxidation experiments were conducted on the type of graphite to be used in the EGCR. Data given in Table III yield the following rate expressions.

$$\text{Air-Graphite} \quad r = 6.97 \times 10^{10} e^{-50,800/RT} \text{ gram/gram hour}$$

$$\text{Oxygen-Graphite} \quad r = 1.64 \times 10^{12} e^{-54,600/RT} \text{ gram/gram hour}$$

Arrhenius plots of these data are shown in Figure 5. Experimental error at the 95 per cent confidence level in the air-graphite experiments was ± 46 per cent and ± 66 per cent in the oxygen-graphite experiments. If an activation energy of 48.4 kcal/mole is assumed on the basis of the kinetic study, the air-graphite rate equation becomes

$$r = 4.30 \times 10^{10} e^{-48,400/RT} \text{ gram/gram hour.}$$

An average additional error of 2.8 per cent and a maximum additional error of 8.9 per cent is thereby introduced.

The dih purity of EGCR graphite is $+0.74 \pm 0.03$, and the apparent density is 1.71 g/cm^3 , as compared to 0.854 dih and 1.70 g/cm^3 for CSF. Trace quantities (≤ 100 ppm) of boron and vanadium which could have caused the pitting shown in Figure 4 have been identified spectrographically.

Effect of Prior Oxidation

Oxidation rates are also influenced by prior oxidation as verified by observation of graphite weight loss as a function of time. In Figure 6 it may be noted that the rate increases steadily through approximately the first 5 per cent burnoff of the sample, and then is constant over a wide range. Apparently the concentration of available sites increases as pores are opened, and then remains constant until the geometric area of the sample is substantially reduced (≥ 70 per cent burnoff). The duration of the induction period appears to depend on the magnitude of the rate. At low temperatures and oxidation rates it is less than 1 per cent burnoff, while at 650 C or above it may constitute up to the first 10 per cent (Figure 7).

TABLE III

OBSERVED OXIDATION RATES FOR EGCR GRAPHITE,
PREDRIED FLOWING GAS (2.0 cfh)

<u>Temperature, C</u>	<u>Rate, (hr⁻¹) x 10³</u>	
	<u>Air</u>	<u>O₂</u>
525	1.01	2.42
550	3.38	7.25
570		12.9
575	6.42	
600	13.3	45.0, 32.5
625	29.8	16.3
650	99.9	

Least Squares Analysis Yields:

Air-Graphite:

$$r = 6.97 \times 10^{10} e^{-50.8 \times 10^3 / RT} \text{ (hr}^{-1}\text{)} \pm 24 \text{ per cent}$$

Oxygen Graphite:

$$r = 5.06 \times 10^{12} e^{-54.6 \times 10^3 / RT} \text{ (hr}^{-1}\text{)} \pm 32 \text{ per cent}$$

Prior oxidation of graphite would then influence the oxidation rates by reducing or eliminating the induction period. Rate data given in this report were all calculated over ranges of constant rate, i. e., after the induction period.

Effect of Gamma Flux

The possibility exists that runaway oxidation in a reactor could be influenced by the effect of the residual gamma flux. A high intensity gamma flux would cause ionization and excitation of oxygen molecules and creation of such highly reactive species as ozone and oxygen atoms. Rates in a gamma field have been observed to be higher than thermal oxidation rates at temperatures

FIGURE 5

Oxidation Rates of EGCR Graphite Compared to CSF Graphite

FIGURE 6

Typical Graphite Weight Loss Curve

FIGURE 7

Induction Period of Oxidation Versus Constant Rate Attained

less than 400 C.⁽¹⁰⁾ The data show that this effect diminishes with increasing temperature because of the low activation energy for reaction with the gamma activated species, and also with the increased rate of recombination in the gas phase.

Oxidation rates are significantly influenced by a Co⁶⁰ gamma flux of 1×10^6 r/hr ($E \simeq 1$ Mev) up to and possibly above 650 C (see Table IV and Figure 8). This gamma radiation is of approximately the same order of energy as that in a reactor but is at least one order of magnitude less intense. Reaction rates observed for the CSF graphite-air reaction in the presence of the gamma radiation followed the relationship:

$$r = 2.78 \times 10^5 e^{-29.1 \times 10^3/RT} \pm 0.34 \text{ r grams/gram hour}$$

from 485 C to 635 C. Thus, the apparent activation energy for the process was 29 kcal/mole in a 10^6 r/hr gamma flux. Approximately the same reaction order with respect to oxygen is observed in these experiments as in thermal oxidation.

Effect of Prior Neutron Irradiation of the Graphite

Neutron irradiation could influence oxidation rates by causing lattice disorder in the graphite and an increase in active carbon sites. Graphite irradiated at low temperatures (< 250 C) was observed to oxidize more rapidly than unirradiated graphite.⁽¹⁰⁾ However, these data have doubtful application for high temperature reactors since annealing occurs during high temperature irradiation and causes damage to be less for an equal exposure.

Experiments were conducted in the laboratory on graphite which had been irradiated at 550 C prior to oxidation since it was felt that this procedure would simulate conditions in a gas cooled reactor after a scram. Analysis of data in Appendix I indicates exposures of 4×10^{19} nvt ($E > 0.18$ Mev) at 550 C did not affect oxidation rates. This is not surprising since dimensions of the graphite and crystal lattice spacing do not change appreciably because of this exposure.⁽¹¹⁾

TABLE IV
OXIDATION OF CSF GRAPHITE
IN THE GAMMA FACILITY (Co⁶⁰ Source)

Flux 1×10^6 r/hr

Air		Oxygen	
Temperature (C)	Rate, (hr ⁻¹) $\times 10^3$	Temperature (C)	Rate, (hr ⁻¹) $\times 10^3$
635	30.6	610	48.9
620	30.4	560	16.1
			16.2
			30.8
610	23.7		
585	9.81	535	5.40
			11.8
555	4.68		
485	1.62	510	3.04

Air:

$$r = 2.78 \times 10^5 e^{-29.1 \times 10^3/RT} \text{ (hr}^{-1}\text{)} \pm 34 \text{ per cent}$$

Oxygen:

$$r = 9.55 \times 10^7 e^{-37.4 \times 10^3/RT} \text{ (hr}^{-1}\text{)} \pm 45 \text{ per cent}$$

FIGURE 8

Arrhenius Plot of CSF Graphite Oxidation
in the Presence and Absence of 1×10^6 r/hr Gamma Flux

CONCLUSIONS

Since graphite oxidation at one atmosphere pressure has been demonstrated to undergo no shifts in mechanism up to 650 C, data from lower temperature experiments could be extrapolated into this higher range. However, the wide difference in chemical reactivity between various nuclear graphites precludes the use of a particular rate equation for all types of graphite.

Neutron bombardment in high temperature reactors is expected to influence oxidation much less than in low temperature reactors. However, data are based on relatively low exposures, and experiments will be repeated on more highly damaged graphite.

Gamma radiation has a marked influence on oxidation rates up to 650 C and perhaps at higher temperatures. Further experiments are planned to investigate the effect of gamma intensity and energy on oxidation.

ACKNOWLEDGMENTS

The author is indebted to W. L. Nicholson and R. L. Buschbom of Operations Research and Synthesis Operation for design and analysis of the factorial experiment used in this study. He is also grateful to S. E. Nichols for capable assistance in all phases of the investigation.

APPENDIX I DETERMINATION OF THE ACTIVE ZONE

The active zone is that fraction of a sample which is reacting as rapidly as the surface. This fraction (η) approaches unity for a Zone I reaction since all active sites are theoretically available to the oxidant. The method of Robinson⁽¹²⁾ is used to test the sample geometries used.

Case I: Hollow Cylinder, Infinitely Long, with Both Surfaces Exposed to Reacting Gas

$$\eta = \frac{2}{\phi_b^2 - \phi_a^2} \frac{[(I_{O_b} - I_{O_a})(\phi_a K_{1_a} - \phi_b K_{1_b}) + (K_{O_a} - K_{O_b})(\phi_b I_{1_b} - \phi_a I_{1_a})]}{I_{O_b} K_{O_a} - I_{O_a} K_{O_b}}$$

where $r_a = 0.125 \text{ in.} = 0.318 \text{ cm}$

$r_b = 0.218 \text{ in.} = 0.541 \text{ cm}$

$d = \text{depth of oxidation}$

$= 0.033 (T/273)^{0.38} r^{-1/2} \text{ cm}$

$= 0.42 \text{ cm at } 600 \text{ C; } 0.146 \text{ cm at } 700 \text{ C}$

$r = \text{weight loss rate (hr}^{-1}\text{) at } 600 \text{ C}$

$= 1.5 \times 10^{-2} \text{ hr}^{-1}$

$\phi_a = r_a/d = 0.318/0.42 = 0.757$

$\phi_b = r_b/d = 0.541/0.42 = 1.29$

I_{ij}, K_{ij} are modified Bessel functions of the first and second kind, respectively, of order i for case j .

Then:

$$\begin{aligned} \eta &= \frac{2}{1.29 - 0.757} \frac{[(1.461 - 1.150)[(0.757)(0.9311) - 1.29(0.3782)]}{(1.461)(0.6012)} \\ &\quad + \frac{(0.6012 - 0.2820)[(1.29)(0.788) - 0.757(0.4081)]}{- (1.150)(0.2820)} \\ &= 0.970 \end{aligned}$$

Since this is nearly unity, it may be concluded that the reaction was homogeneous in depth, and weight loss experiments at these temperatures were valid determinations of Zone I oxidation rates.

Case II: Infinite Cylinder 0.426 Inch in Diameter Oxidized at 600 C

$$\phi = \frac{0.541}{0.42} = 1.29$$

$$\eta = \frac{2}{\phi} \frac{I_1(\phi)}{I_0(\phi)} = \frac{(2)(0.7888)}{1.29(1.4611)} = 0.837$$

Thus, in the factorial experiment, a 14 per cent reduction in the fraction of reacting sample volume is calculated to result from the introduction of cylindrical samples.

APPENDIX II
ANALYSIS OF VARIANCE
OF FACTORIAL EXPERIMENT DATA*

T = Temperature at four levels

F = Flow rate at two levels

N = Neutron exposure at two levels

R = Surface-to-volume ratio at two levels

Basis: (1) 2^3 factorial in 4 units (1/2 replicate), 16 observations

(2) Defining Contrast FNR

Variables: :

T: $t_1 = 400$, $t_2 = 450$, $t_3 = 500$, $t_4 = 550$ C

F: $f_0 = 0.2$, $f_1 = 2.0$ scfh

N: $n_0 = 0$, $n_1 = 4 \times 10^{19}$ nvt

R: $r_0 = 8 \text{ cm}^{-1}$ (cylinder), $r_1 = 20 \text{ cm}^{-1}$ (sleeve)

Data:

<u>Experiment</u>	<u>Rate,</u> <u>(hr⁻¹) x 10⁵</u>	<u>Experiment</u>	<u>Rate,</u> <u>(hr⁻¹) x 10⁵</u>
$t_0^f n_0^r r_0$	11.9	$t_2^f n_0^r r_0$	1120
$t_0^f n_1^r r_0$	0.95	$t_2^f n_1^r r_0$	689
$t_0^f n_0^r r_1$	12.8	$t_2^f n_0^r r_1$	260
$t_1^f n_0^r r_0$	2.6	$t_2^f n_1^r r_1$	836
$t_1^f n_0^r r_0$	13.0	$t_3^f n_0^r r_0$	5600
$t_1^f n_1^r r_0$	17.9	$t_3^f n_1^r r_0$	5220
$t_1^f n_1^r r_0$	28.0	$t_3^f n_0^r r_1$	4710
$t_1^f n_1^r r_1$	10.3	$t_3^f n_1^r r_1$	3770

* The general method outlined by Bennett and Franklin⁽¹³⁾ is used in the analysis of the data.

Estimated Effects:

1. All main effects each confounded with a single second order interaction.
2. All first order interactions involving temperature each confounded pairwise with a second order interaction not involving temperature.
3. All first order interactions not involving temperature each confounded pairwise with a second order interaction involving temperature.
4. All second order interactions involving temperature confounded pairwise.
5. Specifically, the effects thought to be of importance are confounded with alias effects as follows:

<u>Effect</u>	<u>Alias</u>
t	tfnr or fnr
f	tnr
n	tfr
r	tfn

The signs employed in combining observations to obtain estimates of effects and interactions follow.

<u>FOR DATA SETS I AND II</u>								<u>FOR DATA SETS III AND IV</u>							
	<u>F</u>	<u>N</u>	<u>R</u>	<u>FN</u>	<u>FR</u>	<u>NR</u>	<u>FNR</u>		<u>F</u>	<u>N</u>	<u>R</u>	<u>FN</u>	<u>FR</u>	<u>NR</u>	<u>FNR</u>
f	+	-	-	-	-	+	+	(1)	-	-	-	+	+	+	-
n	-	+	-	-	+	-	+	fn	+	+	-	+	-	-	-
r	-	-	+	+	-	-	+	fr	+	-	+	-	+	-	-
fnr	+	+	+	+	+	+	+	nr	-	+	+	-	-	+	-

- (3) Test all of these four treatment observations at each level of T.

(4) Data

SET I			SET II		
Experiment	Rate, (hr ⁻¹) x 10 ⁶	Log ₁₀	Experiment	Rate, (hr ⁻¹) x 10 ⁶	Log ₁₀
t ₀ ^f n ₀ r ₀	119	2.07555	t ₂ ^f n ₀ r ₀	1120	3.04922
t ₀ ^f n ₁ r ₀	9.5	0.97772	t ₂ ^f n ₁ r ₀	689	2.83822
t ₀ ^f n ₀ r ₁	128	2.10721	t ₂ ^f n ₀ r ₁	260	2.41497
t ₀ ^f n ₁ r ₁	<u>26.0</u>	<u>1.41497</u>	t ₂ ^f n ₁ r ₁	<u>836</u>	<u>2.92221</u>
Σ	282.5	6.57545	Σ	2905	11.22462

SET III			SET IV		
t ₁ ^f n ₀ r ₀	130	2.11394	t ₃ ^f n ₀ r ₀	5600	3.74819
t ₁ ^f n ₁ r ₀	179	2.25285	t ₃ ^f n ₁ r ₀	5220	3.71767
t ₁ ^f n ₀ r ₁	280	2.44716	t ₃ ^f n ₀ r ₁	4710	3.67302
t ₁ ^f n ₁ r ₁	<u>103</u>	<u>2.01284</u>	t ₃ ^f n ₁ r ₁	<u>3770</u>	<u>3.57634</u>
Σ	692	8.82679	Σ	19300	14.71522

(5) Substitute log r data into appropriate sign table (I or II) and

	<u>I</u>	<u>F</u>	<u>N</u>	<u>R</u>
t ₀	6.57545	0.40559	-1.79007	0.46891
t ₁	8.82679	0.57323	-0.29541	0.09321
t ₂	11.22462	0.71824	-0.29624	-0.55026
t ₃	14.71522	0.06616	-0.12720	-0.21650

(6) Determine mean logarithmic value for sum of squares of observations of effects and interactions according to:

$$\frac{x^2}{r} - \frac{(\sum x)^2}{16} = \frac{4\sum x^2 - (\sum x)^2}{16}$$

<u>I</u>	<u>F</u>	<u>N</u>	<u>R</u>
2.58388	0.06333	0.21222	0.03613
<u>T</u>	<u>TF</u>	<u>TN</u>	<u>TR</u>
9.09666	0.05902	0.81934	0.14193

(7) Analysis of Variance

<u>Effect of Interaction</u>	<u>Degrees of Freedom</u>	<u>Sum of Squares</u>	<u>Mean Square or Variance</u>
T	3	9.09666	3.03222
F	1	0.06333	0.06333
N	1	0.21222	0.21222
R	1	0.03613	0.03613
TF	3	0.05902	0.01967
TN	3	0.61934	0.20645
TR	<u>3</u>	<u>0.14193</u>	0.04731
	15	10.22863	

On the basis of the relative magnitude of the mean square values, temperature is, as expected, a very significant effect. N and TN could possibly be significant and must be tested. To accomplish this, variance from all terms other than T, N and TN are considered error and combined.

<u>Effect</u>	<u>df</u>	<u>MS</u>
T	3	3.03222
N + TN	4	0.20789
Error	8	0.03755

Experimental error variance is 0.03755.

Then $s^2 = 0.03755$

$\log s = 0.19378 = 1$

$s = 1:56$

Error is then ± 56 per cent

Application of the F test for significance with 4 and 8 degrees of freedom:

$$F = \frac{s_1^2}{s_2} = \frac{0.20789}{0.03755} = 5.536 \quad (95 \text{ per cent})$$

$$F_{4,8} = 4.07$$

It would then appear that either neutron exposure or the interaction between exposure and temperature would exert a significant influence on oxidation rates. Further analysis of variance of these factors:

$$\frac{s^2_{T}}{s^2_{TN}} = \frac{0.21222}{0.20645} = 1.0279$$

where $F_{1,3} = 10.1$

would indicate the noted effect to be due to the exposure-temperature interaction rather than any significant effect from exposure alone.

A significant temperature-exposure interaction, while possible, would be highly unlikely. It was therefore decided to reanalyze the data excluding the lowest temperature level, where results appeared very scattered. Then, on the basis of 12 observations at t_1 , t_2 , and t_3

<u>Effect</u>	<u>df</u>	<u>SS</u>	<u>MS</u>
T	2	4.38395	2.19197
F	1	0.07073	0.07073
N	1	0.01593	0.01593
R	1	0.02986	0.02986
TF	2	0.05861	0.02930
TN	2	0.04646	0.02323
TR	2	0.05177	0.02588

Using these data, any significant influence of N or TN has disappeared. The only effect in this analysis other than temperature which could possibly influence oxidation is flow; however, on analysis

<u>Effect</u>	<u>df</u>	<u>s²</u>
T	2	2.19197
F	1	0.07073
Error	8	0.02532

Then $F = \frac{0.07073}{0.02532} = 2.7934$

But $F_{1,8} = 5.32$ (95 per cent)

Flow variation does not significantly influence oxidation rates. Hence, it may be concluded that none of the variables or interactions, other than temperature, significantly influence oxidation rates.

Error: log

$$s^2 = 0.02532$$

$$s = 0.159$$

Experimental Error = ± 44 per cent

REFERENCES

1. Nichols, P. F. "Adsorption Cross Section of Graphite," Nuclear Science and Engineering, Vol 7: 395-399. May, 1960.
2. Walker, P. L., Jr., F. Rusinko, Jr. and L. G. Austin. "Gas Reactions of Carbon," Advances in Catalysis XI: 133-221. New York: Academic Press, 1959.
3. Arthur, J. R. "Reactions Between Carbon and Oxygen," Trans. Faraday Soc., 47: 164-178. 1951.
4. Laidler, K. L. Chemical Kinetics, p. 14. New York: McGraw-Hill Book Company, 1950.
5. Strickland-Constable, R. F. "The Interaction of Oxygen and Carbon Filaments at High Temperatures," Trans. Faraday Soc., 40: 333-343. 1944.
6. Day, R. J. Kinetics of the Carbon-Oxygen Reaction at High Temperatures (Thesis). Pennsylvania State College, 1949.
7. Blyholder, G. and H. Eyring. "Kinetics of Graphite Oxidation," J. Phys. Chem., 61: 682-688. 1957.
8. Gulbransen, E. A. and K. F. Andrews. "Reactions of Artificial Graphite with Oxygen," Ind. Eng. Chem., 44: 1034. 1952.
9. Clark, T. J. Gas Reactions. I. Thermal and Microwave Oxidation of Various Reactor Grade Graphites, HW-63855. 1960.
10. Kosiba, W. L. and G. J. Dienes. "The Effect of Displaced Atoms and Ionizing Radiation on the Oxidation of Graphite," Advances in Catalysis IX: 398-405. New York: Academic Press, 1957.
11. Davidson, J. M., E. M. Woodruff and H. M. Yoshikawa. "High Temperature Radiation Induced Contraction in Graphite" in Proceedings of the Fourth Conference on Carbon. New York: Pergamon Press, 1960.
12. Robinson, P. J. The Effects of Diffusional Control of Oxidation of Graphite on the Highest Safe Temperature in Air, UK AEA IGR 143(RD/W).
13. Bennett, C. A. and N. L. Franklin. Statistical Analysis in Chemistry and the Chemical Industry, p. 496. New York: John Wiley & Sons, 1954.

INTERNAL DISTRIBUTION

Copy Number

1	F. W. Albaugh
2	J. A. Ayres
3	D. E. Baker
4	R. W. Benoliel
5 - 10	R. E. Dahl
11 - 51	D. R. de Halas
52	R. C. Giberson
53	L. A. Hartcorn
54	J. L. Jackson - H. H. Yoshikawa
55	C. E. Love
56	W. C. Morgan
57	R. E. Nightingale
58	R. E. Olson
59	J. W. Riches
60	B. A. Ryan
61 - 63	R. K. Sharp
64	F. W. Woodfield
65	E. M. Woodruff
66	R. E. Woodley
67	300 File
68	Record Center
69 - 71	Extra
72	G.E. Technical Data Center, Schenectady

EXTERNAL DISTRIBUTION (Special)

73	Aerojet General Nucleonics, San Ramon, Calif. Attn: G. W. Titus
74	Argonne National Laboratory Attn: R. M. Adams
75 - 76	AEC - Division Reactor Development, Washington, D.C. Attn: R. E. Pahler and I. F. Zartman
77 - 78	AEC-HOO Attn: J. M. Musser HOO Technical Information Library
79 - 80	AEC-OROO, Oak Ridge Tenn. Attn: D. F. Cope and W. J. Larkin
81	Allis-Chalmers Manufacturing Company Attn: W. F. Banks and D. A. Lampe
82	Armour Research Foundation Attn: C. W. Boquist
83	Brookhaven National Laboratory Attn: D. H. Gurinsky
84 - 86	General Atomic Division San Diego, Calif. Attn: R. B. Duffield, W. Kosiba and R. A. Meyer

EXTERNAL DISTRIBUTION (Special)

Copy Number

87	General Electric Company, MPD, Detroit, Mich. Attn: T. J. Clark
88	General Electric Research Laboratories Attn: E. R. Stover
89	General Nuclear Engineering Corp., Dunedin, Florida Attn: W. A. Maxwell
90	Great Lakes Carbon Corp., Niagara Falls, N. Y. Attn: L. H. Juel
91	Kaiser Engineers, Oakland, Calif. Attn: P. D. Bush
92	National Carbon Company, Cleveland, Ohio Attn: W. P. Eatherly
93 - 95	Oak Ridge National Laboratory Attn: F. L. Carlsen, R. A. Charpie and J. O. Kolb
96	Speer Carbon Co., Niagara Falls, N. Y. Attn: W. E. Parker
97	The Marquardt Corporation, Van Nuys, Calif. Attn: D. W. Baries
98	Pennsylvania State University Attn: P. L. Walker, Jr.
99	Wright-Patterson AFB, Ohio Attn: R. H. Wilson, Capt.

EXTERNAL DISTRIBUTION

Number of Copies

3	Aberdeen Proving Ground
1	Aerojet-General Corporation
1	Aerojet-General Nucleonics
2	Air Force Special Weapons Center
2	ANP Project Office, Convair, Fort Worth
1	Alco Products, Inc.
1	Allis-Chalmers Manufacturing Company
1	Allis-Chalmers Manufacturing Company, Washington
1	Allison Division-GMC
1	Argonne Cancer Research Hospital
10	Argonne National Laboratory
1	Army Ballistic Missile Agency
2	Army Chemical Center
1	Army Environmental Hygiene Agency
1	Army Medical Research Laboratory
1	Army Signal Research and Development Laboratory
1	Atomic Bomb Casualty Commission
1	AEC Scientific Representative, France
1	AEC Scientific Representative, Japan
3	Atomic Energy Commission, Washington
4	Atomic Energy of Canada Limited
4	Atomics International
2	Babcock and Wilcox Company
2	Battelle Memorial Institute
1	Beryllium Corporation
4	Brookhaven National Laboratory
1	Brush Beryllium Company
1	Bureau of Medicine and Surgery
1	Bureau of Mines, Albany
1	Bureau of Mines, Salt Lake City
1	BUWEPSREP, Goodyear Aircraft, Akron
1	Bureau of Ships (Code 1500)
1	Chicago Operations Office
1	Chicago Patent Group
1	Combustion Engineering, Inc.
1	Combustion Engineering, Inc. (NRD)
1	Committee on the Effects of Atomic Radiation
1	Defence Research Member
1	Denver Research Institute
1	Division of Raw Materials, Washington
1	Dow Chemical Company (Rocky Flats)
3	duPont Company, Aiken
1	duPont Company, Wilmington
1	Edgerton, Germeshausen and Grier, Inc., Goleta
1	Edgerton, Germeshausen and Grier, Inc., Las Vegas
1	Frankford Arsenal

EXTERNAL DISTRIBUTION (contd.)

Number of Copies

1	General Atomic Division
2	General Electric Company (ANPD)
1	General Electric Company, St, Petersburg
1	Glasstone, Samuel
2	Goodyear Atomic Corporation
1	Grand Junction Operations Office
1	Hawaii Marine Laboratory
1	Hughes Aircraft Company
2	Iowa State University
1	Jet Propulsion Laboratory
1	Johns Hopkins University (ORO)
2	Knolls Atomic Power Laboratory
2	Los Alamos Scientific Laboratory
1	Mallinckrodt Chemical Works
1	Maritime Administration
1	Martin Company
1	Massachusetts Institute of Technology (Hardy)
1	Massachusetts Institute of Technology (Thompson)
1	Monsanto Chemical Company
1	Mound Laboratory
1	NASA Lewis Research Center
1	National Bureau of Standards
1	National Bureau of Standards (Library)
1	National Lead Company of Ohio
1	Naval Medical Research Institute
3	Naval Research Laboratory
1	New Brunswick Area Office
1	New York Operations Office
1	Northern Research and Engineering Corporation
1	Nuclear Development Corporation of America
1	Nuclear Materials and Equipment Corporation
1	Nuclear Metals, Inc.
1	Oak Ridge Institute of Nuclear Studies
6	Office of Naval Research
1	Office of Naval Research (Code 422)
1	Office of Ordnance Research
1	Office of the Chief of Research and Development
1	Office of the Surgeon General
1	Ordnance Materials Research Office
1	Ordnance Tank-Automotive Command
1	Patent Branch, Washington
4	Phillips Petroleum Company (NRTS)
1	Picatinny Arsenal
1	Power Reactor Development Company
4	Pratt and Whitney Aircraft Division
1	Princeton University (White)

EXTERNAL DISTRIBUTION (contd.)

Number of Copies

2	Public Health Service
1	Public Health Service, Las Vegas
1	Public Health Service, Montgomery
1	Purdue University
1	Quartermaster Food and Container Institute
1	Radiation Applications, Inc.
1	Sandia Corporation, Albuquerque
1	Sandia Corporation, Livermore
1	Sylvania Electric Products, Inc.
1	Technical Research Group
3	Union Carbide Nuclear Company (ORGDP)
4	Union Carbide Nuclear Company (ORNL)
1	Union Carbide Nuclear Company (Paducah Plant)
1	USAF Project RAND
1	U. S. Geological Survey, Denver
1	U. S. Geological Survey, Menlo Park
1	U. S. Geological Survey, Naval Gun Factory
1	U. S. Geological Survey, Washington
1	U. S. Geological Survey, WR Division
1	U. S. Naval Hospital
1	U. S. Naval Postgraduate School
1	U. S. Naval Radiological Defense Laboratory
1	U. S. Patent Office
1	University of California at Los Angeles
2	University of California, Berkeley
2	University of California, Livermore
1	University of Puerto Rico
1	University of Rochester
1	University of Utah
1	University of Washington (Donaldson)
1	Walter Reed Army Medical Center
1	Watertown Arsenal
2	Westinghouse Bettis Atomic Power Laboratory
1	Westinghouse Electric Corporation
3	Wright Air Development Division
1	Yankee Atomic Electric Company
325	Division of Technical Information Extension
75	Office of Technical Services, Washington