EFFECT OF OXIDIZING ENVIRONMENT ON THE STRENGTH AND OXIDATION KINETICS OF HTGR GRAPHITES

PART I:
REACTIVITY AND STRENGTH LOSS OF H451,
PGX and IG-11 GRAPHITES

M. Eto and F.B. Growcock

September 1981

MASTER

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$$S/S_0 = \alpha(\rho/\rho_0)^\beta + (1-\alpha)(\rho/\rho_0)^\delta$$

ABSTRACT

The effects of oxidizing atmosphere and temperature on the reactivities and strengths of PGX, H451 and IG-11 were examined. Preliminary measurements of the oxidation kinetics of these graphites in H_2O -, CO_2 - and O_2 -containing atmospheres indicated that the reactivities of H451 graphite toward O_2 and H_2O are quite similar to those of IG-11 graphite. The apparent activation energy for oxidation of these in O_2 were estimated to be ~ 175 kJ/mol while that in H_2O is probably ~ 200 kJ/mol. The apparent activation energy of IG-11 graphite oxidized in CO_2 is 255 ± 18 kJ/mol. PGX graphite was found to be quite variable in its reactivity toward H_2O . A linear dependence with $[\text{Fe}]$ was determined, but other intrinsic properties were found to affect its absolute reactivity by as much as a factor of X50. Explanations were advanced for observed anomalies in flow rate and burnoff dependence of the PGX graphite reaction rate in H_2O . Apparent activation energies for PGX graphite oxidation were estimated to be $E_a(\text{O}_2) \sim 165$ kJ/mol; $E_a(\text{H}_2\text{O}/\text{H}_2) = 85 - 250$ kJ/mol, with a median value of 240 kJ/mol; and $E_a(\text{CO}_2) \sim 229 \pm 12$ kJ/mol.

The loss of compressive strength incurred by PGX graphite after oxidation in 2% O_2/N_2 was almost identical to that lost in air, but this was significantly greater than the loss of strength incurred in 2% $\text{H}_2\text{O}/\text{He}$ and 2% CO_2/He . A similar trend was found for loss of tensile strength. The results for H451 graphite oxidized in 2% $\text{H}_2\text{O}/\text{He}$ and 2% CO_2/He and the results for IG-11 graphite oxidized in 2% O_2/N_2 , 2% $\text{H}_2\text{O}/\text{He}$ and 2% CO_2/He were similar to those found for oxidation of PGX graphite in 2% $\text{H}_2\text{O}/\text{He}$ and 2% CO_2/He . A mechanism is proposed to explain the apparently discordant result for PGX graphite in O_2 -containing atmospheres.

The dependence of strength on burnoff was found to be independent of oxidation temperature in the chemical reaction control regime. Attempts to fit strength-burnoff data to a standard expression were only partially successful. A new expression which represents the available data much better is proposed; and its physical basis is briefly discussed.

1. INTRODUCTION

The effect of thermal oxidation on the strength of nuclear graphite is believed to be of utmost concern for the safety analysis and design of high temperature gas-cooled reactors (HTGR's). Graphite is used as a structural material, as well as moderator and reflector in HTGR's, and may suffer structural degradation via oxidation by impurity gases in the helium coolant during normal reactor operation or following an accident that leads to depressurization.¹

Although the relationship between strength and oxidation has been studied by a number of investigators²⁻¹⁹, in most cases the nature of the oxidant has been ignored. The primary focus of this report is a study of the strength of several HTGR graphites oxidized in various atmospheres. Understanding the role played by the oxidant was a major goal of this investigation; toward this end, a limited study of the kinetics of these oxidation reactions was also undertaken.

2. EXPERIMENTAL

2.1 Materials

The graphites used in this study were mainly grades H451 (Great Lakes Carbon Corporation) and PGX (Union Carbide Corporation). IG-11 graphite, an isostatically molded graphite manufactured by Toyo Tanso Co., Ltd. of Japan was also used in the experiment; this is one of the candidate materials for the core and core support parts of the Japanese experimental VHTR. Some properties of these graphites are summarized in Table I. Impurity distributions are given in Table II. Few data are available for loq 13H6-1 of PGX graphite; the manufacturer's value for ash content is 0.32%, [Fe] = 0.14% and ultimate tensile strength = 10.8 (WG), 8.65 (AG) MN/m², where "WG" is with the grain, or axial direction and "AG" represents against the grain, or radial direction.

Cylindrical compressive specimens 19.05 mm ϕ by 38.10 mm length and 12.7 mm ϕ by 25.4 mm length were used in the present study. The 19.05 mm ϕ specimens of PGX graphite were machined from a half-moon shaped block 48 cm in

radius and 9 cm thick which was cut from a mid-length (ML) portion of a production grade block (29N6-2) ca. 127 cm ϕ by 196 cm length. The 19.05 mm ϕ specimens of H451 graphite were machined from a half-moon shaped block (46 cm ϕ by 15 cm thickness) which was cut from a mid-length portion of a production grade block (from Lot 426) 86 cm in length. The longitudinal axis of the H451 specimens was parallel to the grain, while the axis of the PGX specimens was perpendicular to it.

Table 1

Physical and Mechanical Properties of Graphites
Examined in this work

	IG-11	H451 ^b		PGX	
		WG	AG	WG	AG
Density(g/cm ³) ^a	1.75	1.76		1.78	1.74
Modulus of Elasticity ^a (GN/m ²)	9.85	[8.51]	[7.38]	5.8-6.4	6.9-7.4 (8D5-3 & 20K5-1) ^d
Tensile Strength ^a (MN/m ²)	24.4	15.2 [16.7]	[13.7]	7.0 9.9	-- (2V4-1) 10.0(29N6-2)
Compressive Strength ^a (MN/m ²)	71.5	[55.3]	52.7 (Lot 478)	29.3 41.0	32.8(2V4-1) 43.0(29N6-2)
Ash Content (%) ^a	<0.01	<0.0033		0.24	
Open Porosity (%) ^c	--	20.2		18.0	
Viscous Flow Permeability Coefficient (cm ²)	(~6x10 ⁻¹¹) ^a	8x10 ⁻¹¹		6x10 ⁻¹⁰	
B.E.T. Surface Area (m ² /g)	2.8	2.1 ^c - 3.4		0.7 ^c (2V4-1) 2.1 (8D5-3)	
Method of Manufacture	Isostatic Molding	Extrusion		Conventional Molding	
Manufacturer	Toyo Tanso	Great Lakes Carbon		Union Carbide	

^aManufacturer's values

^bValues in brackets are averages obtained by the supplier, General Atomic Co. (GA), for lot 426. See ref. 19.

^cMeasured by Micromeritics Corp.

^dMeasured by GA, ref. 20.

Table II
Elemental Impurity Concentrations in PGX Graphite^a ppm

Manufacturer Log Number	Fe	V	Ti	Ca	Ba	Sr	Ni	Cu	S
2V4-1 (EL) ^a	20-1200	10-30	20-66	14-66	1.5-21	19-156	1-32	0.6-3.2	97-243
29N6-2(EL) ^a	7-466	18-56	39-128	13-196	2.1-4.6	41-1700	0-3.9	0.1-2.0	80-3910
29N6-2(ML) ^a	19-434	26-82	55-182	0-19.3	1.8-4.0	9.1-48.2	0.7-12.2	0.3-1.0	51-98
8D5-3 ^b	40->1000	4-40	20-80	8->1000	40-60	<40	1-40	6-20	100-1100
20K5-1 ^c	40-400	<0.5-40	4-40	<20-100	<0.5-60	<40	<4-10	<1	<2-527
H451 ^d	3.2	0.5	1.3	21.9	(0.5)	(40)	0.14-0.2	(1)	1.5

^aK, Mg, Mn, Al and Si were also analyzed: [K], [Mg] and [Mn] were in the range 1-60 ppm, [AL] ~60-200 ppm and [Si] ~20-400 ppm.

^bAfter Engle, ref. 21.

^cAfter Engle and Beavan, ref. 22. Note: These values and those for 8D5-3 were obtained by spark emission spectroscopy, which the authors warn may be considerably too low.

^dUpper limits from analyses of other preproduction logs from, lot 426 of GA.

Other impurities measured were [Mg] <0.9, [AL] <21.9, [Si] <21.3, [Pb] <7.1 and [B] <2.5.

The reader should note that the impurity distributions in H451 graphite can vary widely: ash content of logs from various lots has been shown to range from 20 to >300 ppm.

The 12.7 mm ϕ cylindrical compressive specimens were cut from H451, PGX and IG-11 graphite blocks. Tensile specimens of graphite grades H451 and PGX measured 12.7 mm ϕ by 76.2 mm length. The longitudinal axis of all the 12.7 mm ϕ H451 and PGX graphite specimens was parallel to the radial direction of their parent blocks; these half-moon shaped blocks measured 43 cm ϕ by 17 cm length (H451) and 54 cm ϕ by 9 cm length (PGX). The block of PGX graphite came from the end-length (EL) of log 13H6-1. In the case of the IG-11 compression specimens, the longitudinal axis was parallel to that of a quadrant-shaped block 36 cm ϕ by 16 cm length.

Thermogravimetric measurements were made with a few PGX graphite specimens; these measured 1.1 cm ϕ by 0.64 cm in length. Prior to use, all the specimens were cleaned ultrasonically in absolute methanol and dried in air at 75 to 80°C for about 10 hr.

2.2 Strength Measurements

Strength measurements of the large compressive specimens were carried out using a Tinius-Olsen Universal Testing Machine with maximum allowable load of ca. 5500 kg at a strain rate of $1.1 \times 10^{-3} \text{ sec}^{-1}$. Tensile tests were also performed with this machine at a strain rate of $5.5 \times 10^{-4} \text{ sec}^{-1}$ using a standard method developed by previous investigators⁸ and shown in Figure 1. The small compressive specimens were tested by the ASTM method using an Instron screw-driven test machine (maximum allowable load 4600 kg) operating at a strain rate of $3.3 \times 10^{-4} \text{ sec}^{-1}$.

2.3 Oxidation

Oxidation of the tensile and compressive specimens was carried out in a quartz tube through which various atmospheres, including air, 2% O_2/N_2 , 2% CO_2/He or 2% $\text{H}_2\text{O}/\text{He}$ (with and without H_2), were passed, generally at a flow rate of 300 sccm. Higher flow rates were necessary in a few cases (high oxidation rates) to limit conversion of the oxidant to <5%. Gas metering was performed with Aalborg flow controllers which had been calibrated against Tylan electronic flow controllers. The water vapor mixtures were made by pas-

Figure 1. Overview of the Tensile Testing Method Employed in the Present Study.

sing helium with or without hydrogen either over a 9:1 mixture of oxalic acid dihydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$): oxalic acid anhydrate ($\text{H}_2\text{C}_2\text{O}_4$)²³ maintained at 50°C or through a bubbler containing doubly-distilled H_2O which was maintained at ca. 18°C. Both blended mixtures provided water vapor at a concentration of ca. 2%. Reaction temperatures ranged from 400 to 650°C for oxidation in air and in 2% O_2/N_2 , 600 to 900°C for oxidation in 2% CO_2/He and 550 to 900°C for oxidation in 2% $\text{H}_2\text{O}/\text{He}$ with or without H_2 .

Oxidation of the 1.1 cm ϕ by 0.64 cm specimens of PGX graphite was carried out with mixtures of H_2O and He with or without added H_2 in various proportions at flow rates ranging up to 5000 sccm. The effect of high flow rates on $P_{\text{H}_2\text{O}}$ in the reaction zone or on the specimen temperature was negligible. Reaction temperatures were varied from 550°C to 950°C. Airco high purity He and H_2 were blended and passed over Cu turnings kept at ca. 600°C, followed by 13x molecular sieves maintained at -196°C. This procedure lowered the concentrations of O_2 , CO_2 , CO, H_2O and CH_4 to < 1 ppmv in the He/ H_2 mixtures.

2.4 Measurements of Reaction Rate

Reaction rates for oxidation of compressive and tensile specimens in different atmospheres were calculated from the concentrations of the carbon-containing product gases, which were monitored with a Carle Analytical Gas Chromatograph Model 311. Methanation of these gases followed by analysis with an FID gave rise to minimum detectable limits of 20 and 50 ppbv for CO_2 and CO, respectively. All other species were measured with a thermistor TCD. The detectors were calibrated periodically with mixtures of gases of similar composition as that of the product gases. Reaction rates of specimens oxidized in the microbalance were also measured via gas chromatography to corroborate the results from the instantaneous weight change measurements; in some cases, the weight change measurements (thermogravimetric analysis) were used exclusively. The thermogravimetric apparatus used in these experiments is shown schematically in Figure 2.

Figure 2. Schematic of Thermogravimetric Apparatus.

The oxidation rate calculated from the gas chromatography data is given by the weight loss expression

$$-\frac{dW_c}{dt} = \frac{12q}{RT} \sum_i \frac{P_i}{v_i}$$

where W_c is the weight of carbon, q is the flow rate of the gas mixture, P_i is the partial pressure of carbon-containing product species, and v_i is a stoichiometric coefficient (e.g., $v_{CO} = 2$ for $C + CO_2 \rightarrow 2CO$). The mean reaction rate for each oxidation experiment was also estimated from the total weight loss of a specimen and the reaction time.

3. RESULTS AND DISCUSSION

3.1 Oxidation Kinetics

To establish the relative reactivities of IG-11, H451 and PGX graphites for general use, as well as to satisfy the needs of HTGR design engineers, various aspects of the reactions must be investigated separately and then synthesized into kinetic expressions that are valid over the entire working range of experimental parameters. In this study, preliminary measurements were made of the effects of various experimental parameters on the gasification rates of IG-11, H451 and PGX graphites. Most of the data are for PGX graphite, since it is already in use: the core support blocks in the Fort St. Vrain HTGR are PGX graphite.

Flow Rate Dependence:

The effect of flow rate on the oxidation rates of H451 and PGX graphites was investigated using specimens 1.1 cm ϕ by 0.64 cm length. The effect of 0.63% H_2O /8.3% H_2 /He is depicted in Figure 3. Flow rates are given in standard cm^3/min (sccm). The increase of reaction rate with burnoff is responsible for both the hysteresis of the lower curve and the apparent higher rate with added H_2 compared to that without H_2 . Total burnoff was <1%. The hysteresis of the upper curve and the two abrupt increases in the reaction rate during

Figure 3. Effect of Flow Rate on the Rate of Oxidation of an H451 Graphite Specimen.

the course of the experiment are difficult to understand. The runs with a second specimen of H451 graphite (Figure 4) exhibited similar behavior and gave rise to a continuously increasing oxidation rate with increasing flow rate. Under these conditions, conversion of the oxidant decreases rapidly with increasing flow rate, so that at a few hundred cm^3/min , conversion is <2% per pass. Thus, it is surprising that the reaction rate should continue to increase with flow rate even beyond 2,000 cm^3/min . This effect has been observed by others, however, for ATJ²⁴ and H327²⁵ graphites. Under the experimental conditions used for all of the above measurements, the reaction has been assumed to proceed in the chemical-reaction-control temperature regime. The temperature dependence of the reaction rate (discussed later) yields an apparent activation energy at this temperature of ~ 200 kJ/mol. This high activation energy indicates that the reaction either proceeds in the in-pore diffusion limited regime or is a catalyzed process controlled by the chemical reaction. On the other hand, the regular, almost linear, increase in the flow rate implies mass-transfer control through the surface film. Calculations of the diffusion length (the distance at which the oxidant concentration is reduced by 63%) for these experiments indicate that diffusion of the oxidant into the pore network may limit the reaction rate in those cases where the overall rate surpasses 0.1 mg/min (Figures 3, 5 and 6), but should not affect the other cases.

Density profiles of specimens oxidized under conditions similar to those described above indicate that the gasification is a complex process. As will be shown later, burnoff profiles of machined graphite specimens generally exhibit excess burnoff near the surface, which may be attributed to the expanded role played by micropores that open to the exposed surface. At the temperatures used in the flow rate studies, transport of oxidant into the surface micropore network may be expected to be through the surface film; as a result, the apparent activation energy is a weighted average of the activation energy for reaction in the bulk pore network and the activation energy for reaction in the surface micropore network.

The effect of flow rate on the oxidation rate of PGX graphite is, in some cases, even more curious. Three specimens, each containing <100 ppm, 400 ppm and >1000 ppm iron (as measured by Mössbauer spectroscopy) were exposed to

Figure 4. Effect of Flow Rate on the Rate of Oxidation of an H451 Graphite Specimen at 900°C.

Figure 5. Effect of Flow Rate on the Oxidation Rate of a PGX Graphite Specimen Containing ~100 ppm Iron at 950°C in 0.63% H₂O/6.0% H₂/He.

Figure 6. Effect of Flow Rate on the Oxidation Rate at 750°C of a PGX Graphite Specimen Containing ~400 ppm Iron.

Figure 7. Effect of Flow Rate on the Oxidation Rate at 817°C of a PGX Graphite Specimen Containing >1000 ppm Iron.

0.63% H₂O in He, with and without an excess amount of H₂. These results are displayed in Figures 5, 6 and 7. In the absence of added H₂, the rates in every case were relatively independent in flow rate, although some oscillatory behavior was noted. In the presence of H₂, the specimen containing very little iron reacted more slowly at high flow rates than at low ones, while the specimens with larger amounts of iron behaved very much like H451 graphite. This discrepancy was checked by repeating the experiment with incrementally decreasing flow rate: the reaction rate behaved as before. Another specimen containing very little iron was subjected to the same procedure. Although hysteresis was rather pronounced, it, too, displayed an inverse dependence of the reaction rate on flow rate. An explanation for this phenomenon is still lacking.

Reaction Order:

A Langmuir-Hinshelwood kinetics expression is often used to treat oxidation rate data of graphite with O₂, CO₂ and H₂O. In that treatment, the reaction rate is assumed to vary directly with the concentration of oxidant at low surface coverage (low pressure). With increasing pressure or addition of the reaction products, inhibition of the reaction occurs and the rate is no longer linearly dependent on the concentration of oxidant. The reaction order is seen to decrease from 1, which is attributed to occupation of active sites by both the oxidant and the reaction products.²⁶ Desorption of the products is generally assumed to be slower, thus it controls the rate under these conditions. Although variations of this scheme and the resulting rate expression abound, we have found that over limited ranges of concentration and temperature, reaction rate data for IG-11 and H451 graphites can be treated with single expressions based on Langmuir-Hinshelwood mechanisms. PGX graphite, on the other hand, is not amenable to this kind of treatment, so that comparisons of rates among the three graphites must contain strong caveats.

Some data are presented here for the oxidation of PGX graphite, primarily in H₂O/H₂ mixtures in He. A detailed report of PGX graphite oxidation in H₂O/H₂/CO in He is given elsewhere.²⁷

Figure 8. Dependence of the H₂O - PGX Graphite Reaction Rate at 818°C on [H₂O] for a Specimen Containing 1000 ppm.

Oxidation in $\text{H}_2\text{O}/\text{He}$ of PGX graphite specimens from log 2V4-1 containing 100 and 400 ppm iron showed a linear first-order dependence on $[\text{H}_2\text{O}]$ over the range 40-20,000 ppm. These results are displayed in Figure 8. Results for specimens from both logs 2V4-1 and 29N6-2 in $\text{H}_2\text{O}/\text{He}$ with added H_2 ($P_{\text{H}_2}/P_{\text{H}_2\text{O}} \sim 10$) were more like those expected for purer graphites, i.e., first order dependence on $[\text{H}_2\text{O}]$ at low pressures, decreasing to fractional order with increasing $[\text{H}_2\text{O}]$. The dependence of the reaction rate on $[\text{H}_2]$ at several temperatures was examined using a specimen from log 2V4-1 containing ~ 100 ppm iron. These results are shown in Figures 9 and 10. Enhancement of the rate by added H_2 is quite dramatic, especially at 761°C . This enhancement can be attributed to the catalytic effect of iron, the dominant impurity in PGX graphite. Iron has been shown to be catalytically active for oxidation of graphite by H_2O when it is in the elemental (metallic) state.²⁹ The inversion point at low values of $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ corresponds closely to that calculated from thermodynamics to be necessary for reduction of wüstite (Fe_{1-x}O) to α - or β -Fe. The decreasing effect of H_2 on the rate with increasing temperature can be attributed to several factors: reduction of iron by the graphite itself, the larger amount of H_2 formed during the reaction and limitation of the rate by slow diffusion of reactants through the pores. It should be noted that the effect of CO on the oxidation rate of PGX graphite is similar, but not as great, as that of H_2 .

Burnoff Dependence:

The history of a specimen affects, and in many cases determines, its reactivity. The amount of carbon removed, or burnoff, is no exception. It is generally agreed that the oxidation process opens up both existing pores and pores previously closed. At low burnoffs, oxidation opens up very small pores, affecting the macroporosity very little; the active surface area increases greatly during this period, an effect which is expressed as a dramatic rise in the specimen's reactivity. At high burnoffs, increases in the pore dimensions affect the active surface area (ASA) very little, and, in fact, the pores may grow so large as to coalesce (leading to a decrease of the ASA), resulting in little change or a decrease in reactivity. These effects have been seen in all of the graphite grades examined. In Figure 11 and 12 the reactivities of H451 graphite specimens in 2% $\text{H}_2\text{O}/\text{He}$ and in air are seen to

Figure 9. Dependence of the H_2O -PGX Graphite Reaction Rate on $[H_2]$ at 760°C and 660°C; $[H_2O] = 0.64\%$ in He, and the Specimen (oxidized to 6% burnoff) Contained ~100 ppm Iron

Figure 10. Dependence of the H_2O -PGX Graphite Reaction Rate on $[H_2]$ at 956°C and 857°C; $[H_2O] = 0.64\%$ in He, and the Specimen (oxidized to 5% burnoff) Contained ~100 ppm Iron.

Figure 11. Effect of Burnoff on the Reaction Rate of H451 Graphite with 2% H₂O/He.

Figure 12. Effect of Burnoff on the Reaction Rate of H451 Graphite with Air.

Figure 13. Effect of Burnoff on the Reaction Rate of PGX Graphite with Air.

Figure 14. Effect of Burnoff on the Oxidation Rate of a PGX Graphite Specimen Containing ~600 ppm Iron with 0.64% H_2O/He at 920°C.

increase uniformly, an indication that pore development is proceeding smoothly. As shown in Figures 13 and 14, the reactivities of PGX graphite specimens appear to behave similarly. The data in Figure 13 are for several 13H6-1 specimens oxidized in air, while those in Figure 14 are for a 2V4-1 specimen containing ~ 600 ppm iron oxidized in 0.64% H_2O/He . However, other data for PGX graphite indicate that the situation is somewhat more complex than indicated by these results.

Several 13H6-1 specimens were oxidized in 2% H_2O/He ; the reactivities of these specimens, as shown in Figure 15, were observed to increase up to <1% burnoff and then decrease by at least an order of magnitude (no minima were reached in these experiments). A similar experiment (using 0.86% H_2O/He) with a second 2V4-1 specimen, this one containing <40 ppm iron, led to the result shown in Figure 16. Some oscillatory behavior superimposed on a steadily decreasing rate was noted when a PGX graphite specimen from log 29N6-2 (ML) was oxidized in 0.63% H_2O/He with 6.3% H_2 added. This is illustrated in Figure 17. A few large specimens from log 29N6-2 (EL) have shown similar behavior under the same conditions.

The anomalous steadily decreasing rate behavior of PGX graphite has also been seen recently by workers from GA;³⁰ in those experiments, H_2 was added to give $P_{H_2}/P_{H_2O} = 10$. This phenomenon has also been observed by the same workers with H451³¹, H327 and ASR-1RG³² (Sigri) graphites upon exposure to $H_2O/H_2/He$ mixtures. The GA workers have ascribed the phenomenon to slow adsorption of H_2 on the graphites. Many researchers in the field have assumed that adsorption of H_2 on graphite is relatively fast. However, data on the reaction of H_2 with carbons at temperatures as low as 650°C suggest that chemisorption of H_2 on graphite is indeed slow compared to adsorption of oxygen-containing species.^{33,34} Measurements of chemisorption of H_2 on pre-oxidized (to 12% burnoff) re-compacted spectroscopic grade natural graphite (<1 ppm total impurities) at 1100°C indicated that, although a majority of the equilibrium amount of H_2 adsorbed within 2 min., slow uptake of H_2 continued for at least 1 hr;³⁵ hydrogen adsorption data on a high-purity (<40 ppm ash: Ca, Ti ~ 5 ppm each) channel black at 985°C gave a similar result.³⁵ Furthermore, the ASA's calculated for these two materials from H_2 chemisorption data were found to be less than those reported from O_2

Figure 15. Effect of Burnoff on the Reaction Rate of PGX Graphite with 2% H₂O/He. The Curves Serve Only to Indicate the Spread in the Data.²

Figure 16. Effect of Burnoff on the Reaction Rate of a PGX Graphite Specimen Containing <40 ppm Iron with 0.86% H_2O/He at 810°C.

Figure 17. Effect of Burnoff on the Oxidation Rate of a PGX Graphite Specimen Containing <100 ppm Iron in 0.63% $H_2O/6.5\% H_2/He$.

chemisorption at 300°C. Therefore, the slowly declining reaction rates reported here and elsewhere may be attributable to slow adsorption of H₂.

However, reductions in the H₂O oxidation rate of 2 to 3 orders of magnitude have been reported^{31,32} after soak times of 2-14 days in an H₂O/H₂ mixture at 820-980°C; the large magnitude of these rate changes is more in keeping with those expected for catalyst poisoning. In addition, it should be noted that the inhibition of the reaction rate of the channel black discussed above was greater than that of the graphite, which was explained by the differences in ASA's of the materials and chemisorption of H₂ on impurities in the channel black; the latter would result in poisoning their catalytic activity. Finally, in a study on the reaction of a purified (2-8 ppm ash content) nuclear graphite with H₂/H₂O/He mixtures at 790-850°C, preoxidation of the specimens in air at 525°C to 5% burnoff followed by soaking at temperature in purified He for 18-24 hr led to relatively constant reaction rates upon exposure to the reactant mixtures; these exposures were of 8 to 40 hr duration.³⁶ Thus it appears that the nature of the graphite may play an important role in the "declining reaction rate" phenomenon observed here and elsewhere.

Several common threads run through the results obtained for PGX graphite oxidation in H₂O. In the first place, only specimens containing small amounts of impurity iron have been observed during the course of this study to give steadily declining or oscillatory rates. Secondly, steadily declining rates of PGX graphite specimens oxidized in H₂O have been observed with and without added H₂. Thirdly, only specimens which contained small amounts of iron and which were exposed to H₂O with no added H₂ have shown large oscillatory behavior. The anomalous burnoff behavior of PGX graphite can be explained by mechanisms other than the slow adsorption of H₂. Separate mechanisms are advanced to explain the oscillatory rate behavior and the steadily declining rate behavior observed in this work.

Evidence gathered from Mössbauer spectroscopy and SEM/XES maps indicates that the iron impurity in PGX graphite exists in the form of mobile clusters of effective diameter between 300 and 5500 Å.³⁷ Particles in this size range are quite mobile during oxidation.^{38,39}

Examination of PGX graphite specimens from log 2V4-1 revealed that the vast majority of iron clusters (particles) are generally aggregated into bunches which can attain a size of @ 1 mm in equivalent spherical diameter. During catalytic oxidation, there is a strong tendency for the Fe clusters within an aggregate to move in concert, so that the active unit may appear to be the aggregate itself. The strength of the coupling among the iron particles can be quite variable, however, so that during development of an oxidation pit (wormhole) iron particles may be left behind or on the walls of the pit itself. The scenario envisioned for the oscillatory rate behavior mechanism is as follows. An iron aggregate migrates to an active site, where catalytic oxidation ensues; after gasification, the aggregate moves on to another active site. However, the aggregate can be trapped or slowed in a region if it happens to come upon relatively inactive material or if the iron particles become deactivated, e.g. via oxidation by H_2O , whence the reactivity in that locality drops for awhile. In iron-rich specimens the oscillatory behavior is masked, since the probability is very low that all aggregates will be immobilized at the same time. Even in the case where the gaseous environment is oxidizing, the local H_2 or CO concentration may reach sufficiently high levels in the vicinity of some iron particle aggregates that reduction (activation) of these can occur. In iron-poor specimens, however, the probability that a few aggregates will be immobilized at the same time is much higher. It is conceivable that only a handful of iron particle aggregates may be present in the purest of PGX graphite specimens, so that oxidation might lead to the oscillatory rate behavior seen in Figures 16 and 17. Iron X-ray maps of a 1-2 g iron-poor specimen indicate that, indeed, the iron impurity concentrated in three or four spots, each a fraction of a mm in area.

In the second mechanism, iron is active initially, but becomes deactivated either through oxidation or dissolution/carbonization. The former process is much more rapid than the latter processes. A large fraction of the iron in as-received PGX graphite may be in elemental form. Oxidation of iron can account for the rather rapid changes in the rates observed in Figure 13. However, the long downward tails of the curves in both Figures 13 and 14 are similar to those seen in purer graphites and with PGX graphite in the presence of added H_2 . The slowly declining rates can therefore not be attributed solely to effects pertaining to impurity iron. PGX graphite and H451 and H327

graphites from some manufacturing lots have substantial amounts of metallic impurities which are catalytically active as oxides. Some of these are difficult to reduce. Experiments with large specimens of PGX graphite exposed to H_2O in He with an excess of H_2 indicate that the specimens which showed declining rates generally contained substantial amounts of at least one of the following impurities: Ca, Sr, Mg, Mn, Ti, V and S. The presence of one or more of these impurities in a catalytically active form could lead to high rates initially; exposure to H_2O/H_2 mixtures (or H_2O under some conditions) could result in slow reduction, or deactivation, of the catalyst. The evidence is not sufficiently strong yet to permit a choice between the H_2 adsorption mechanism and the catalyst deactivation mechanism. This phenomenon needs to be investigated further since its potential impact for the evaluation of reaction rates and the prediction of burnoffs is great.

Temperature Dependence:

Apparent activation energies, E_a , for oxidation of IG-11, H451 and PGX graphites in various atmospheres have been determined. These are listed in Table III, along with the figure numbers to which one can refer for Arrhenius plots of the data. Uncertainties were calculated assuming 90% confidence limits. One can compare these values with those from the literature. Relatively consistent values have been obtained by a number of investigators for the gasification of very pure carbons.^{26,40} These values are 364 ± 13 kJ/mol for C- CO_2 , 320 ± 50 kJ/mol for C- H_2O and 255 ± 13 kJ/mol for C- O_2 . Impurities, even in trace amounts, can decrease E_a substantially. For nuclear graphites, E_a has been found to vary quite a bit: most values fall in the ranges $E_a(CO_2) = 230-370$ kJ/mol^{24,29,33,41-44}, $E_a(H_2O) = 170-340$ kJ/mol^{1,7,10,24,26,27,29,31,36,40,42,45} and $E_a(O_2) = 145-270$ kJ/mol.^{26,33,37-46}

Workers at GA and JAERI (Japan Atomic Energy Research Institute) have obtained Arrhenius parameters for oxidation of IG-11, H451 and PGX graphites in H_2O/He environments. Workers at GA obtained $E_a(H451) = 195$ kJ/mol³¹ for $P_{H_2O} > 300$ Pa (our experiments were generally conducted with 2% H_2O in He, or $P_{H_2O} \sim 2,000$ Pa) and $E_a(PGX) = 245$ kJ/mol⁵⁷ for $P_{H_2O} \sim 100$ Pa and $P_{H_2} \sim 1000$ Pa. JAERI workers obtained $E_a(IG-11) = 268$ kJ/mol, $E_a(H451) = 247$ kJ/mol and $E_a(PGX) = 209$ kJ/mol for 0.65% H_2O in He.⁵⁸

The JAERI values are not extensive and can only be considered preliminary. Our result for H451 graphite in H₂O is quite close to that of GA and significantly lower than that of the JAERI workers. Our results for PGX graphite logs 2V4-1 and 29N6-2 oxidized in 2% H₂O/20% H₂/He also compare favorably with the GA estimate, while our result for log 13H6-1 is in adequate agreement with the JAERI value, though no H₂ was added in the latter's experiments.

Table III

Apparent Activation Energies for Graphite Oxidation Reactions

<u>Graphite</u> <u>Grade</u>	<u>Atmosphere</u>	<u>Burnoff</u> <u>Range, %</u>	<u>Temperature</u> <u>Range, °C</u>	<u>Apparent</u> <u>Activation</u> <u>Energy, kJ/mol</u>	<u>Figure</u>
IG-11	2%CO ₂ /He	0.38-0.49	750-850	255 ± 18	18
	2%H ₂ O/He	0.14-0.64	760-850	~200 *	-
	2%O ₂ /N ₂	0.54-0.67	445-540	172 ± 15	19
H451	2%H ₂ O/He	0.25-3.12	700-850	207 ± 10	20
	Air	<7.9, <10.2	450-600	197	21
PGX	2%CO ₂ /He	1.5-3.75	750-850	229 ± 10	22
(13H6-1)	2%H ₂ O/20%H ₂ /He	<6.25-<9.05	550-750	~ 189	23
(29N6-2)	0.1-2.0%H ₂ O/ 1.0-20%H ₂ /He	<2%	550-950	240 ± 20	24,25
(2V4-1)	0.1-2.0%H ₂ O/ 1.0-20%H ₂ /He	<2%	650-950	85-250	-
	2%O ₂ /N ₂	1.0-2.8	450-550	~165	26
	Air	<17	450-550	<187	27

* Data obtained for only two (2) specimens.

Figure 18. Arrhenius Plots for IG-11 Graphite Oxidized in 2% CO₂/He.

Figure 19. Arrhenius Plots for IG-11 Graphite Oxidized in 2% O₂/N₂.

Figure 20. Arrhenius Plots for H451 Graphite Oxidized in 2% H₂O/He.

Figure 21. Arrhenius Plots for H451 Graphite Oxidized in Air.

Figure 22. Arrhenius Plots for PGX Graphite Oxidized in 2% CO_2/He .

Figure 23. Arrhenius Plots for PGX Graphite Oxidized in 2% H₂O/20% H₂/He.

Figure 24. Arrhenius Plot for a PGX Graphite Specimen 6 mm ϕ x 10 mm Length Containing 1150 ppm Iron from Union Carbide Log 29N6-2 Oxidized in 0.10% H₂O/1.0% H₂/He.

Figure 25. Arrhenius Plots for Two PGX Graphite Specimens 6 mm ϕ x 10 mm Length from Union Carbide Log 29N6-2 Oxidized in 0.10% H₂O/1.0% H₂/He.

Figure 26. Arrhenius Plots for PGX Graphite
Oxidized in 2% O₂/N₂.

Figure 27. Arrhenius Plots for PGX Graphite Oxidized in Air.

Generally speaking, our results follow the trend $E_a(\text{CO}_2) > E_a(\text{H}_2\text{O}) > E_a(\text{O}_2)$, as expected. The trend with grade of graphite is more nebulous, as the data are less complete; it has been noted, too, that E_a generally decreases with increasing burnoff, so comparison of graphites oxidized to different burnoff levels is difficult.⁵⁹ It does appear that $E_a(\text{IG-11}) > E_a(\text{PGX})$ for any chosen oxidizing gas, but a comparison with H451 is not possible. $E_a(\text{H451})$ for air oxidation may be too high. Some of the data, including this set, were taken such that the rate measurements were made in steps of increasing temperature; the calculated apparent activation energy can be expected to be too high as a result of the effect of burnoff, particularly at low burnoff levels. Those measurements which were grossly affected in this way are shown as maximum values in Table IV.

A comparison of reactivities in O_2 -containing environments gives $R(\text{PGX}) > R(\text{H451}) \sim R(\text{IG-11})$, in keeping with the relative impurity levels of the three graphites. A few experiments with PGX graphite (log 13H6-1) using 2% $\text{H}_2\text{O}/\text{He}$ with no added H_2 gave results which showed that the trend in H_2O is similar to the trend found for O_2 . Over the temperature range 760-850°C, estimates of the rates gave the ratio $R(\text{PGX}):R(\text{H451}):R(\text{IG-11}) = 4:1:1$, in good agreement with the JAERI results. It may be assumed that the trend with 2% $\text{H}_2\text{O}/20\% \text{H}_2/\text{He}$ will be $R(\text{PGX}) \gg R(\text{H451}) \sim R(\text{IG-11})$, as a result of promotion of the iron catalyst in PGX graphite and inhibition of the rates of H451 and IG-11 graphites.

Material Variability:

The dependence of reaction rate on impurity concentration was also of interest, particularly the effect of $[\text{Fe}]$ on the oxidation of HTGR graphites in H_2O -containing environments. PGX graphite disks 6 mm in diameter from three logs were tested extensively with $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ fixed at a value of 10/1. Relative reactivities at a normalized burnoff of 1% were obtained over the water vapor partial pressure range $P_{\text{H}_2\text{O}} = 100 - 2,000 \text{ Pa}$. The results indicated that the reaction rate varies linearly with $[\text{Fe}]$, but the absolute value of the rate strongly depends upon other properties of the material. Relative reactivities of PGX graphite (normalized to the same iron concentration and burnoff) followed the trends given in Table IV.

Table IV

Relative Reactivities of PGX Graphite Specimens

<u>Manufacturer's Log Number</u>	<u>Temperature, °C</u>	<u>Relative Reactivity</u>
2V4-1 (EL)	750	0.4
2V4-1 (EL)	800	2
2V4-1 (EL)	900	60
29N6-2(EL)	800	4
29N6-2(ML)	700	5
29N6-2(ML)	800	100
13H6-1(EL)	700	~ 2
13H6-1(EL)	800	~ 16

These differences in reactivity (a factor of X50 among the specimens tested) can be due to a number of variables, such as other impurities, crystallite size and orientation, and degree of graphitization.

Variability of the reactivities of H451 and IG-11 was quite low: a factor of 2X covered the ranges of reactivity toward CO₂, H₂O or O₂.

Burnoff Profiles:

Radial density profiles of oxidized HTGR graphites were made by machining off thin layers of material from the outer surface and weighing the residual core after each machining step. Burnoff profiles were calculated from the density profiles according to the expressions

$$\text{and } B_i = (\rho_0 - \rho_i) / \rho_0$$

$$B_k = (\rho_0 - \rho_k) / \rho_0$$

where B_i is the fractional burnoff of the residual core after the i^{th} cut, B_k is the fractional local burnoff at that position, ρ_0 is the density before oxidation, ρ_i is the density of the residual core (given by $\frac{4W_i}{\pi d_1^2 l_0}$),

where W_i is the weight of the residual core of diameter d_i and length and ρ_0 is the density of the k^{th} annular section (given by $\frac{4(W_{i-1} - W_i)}{\pi(d_{i-1}^2 - d_i^2)l_0}$).

Local burnoff profiles (and in some cases bulk burnoff, or burnoff of the residual core) for H451 and PGX graphite specimens oxidized in air or 2% H_2O/He are presented in Figures 28, 29 and 31 and Figure 32, respectively. Figure 31 shows a burnoff profile of a "cocoon" specimen, a schematic of which is shown in Figure 30. The core of the cocoon is shielded from the flowing gases; this was intended to minimize any aberrant effects caused by product inhibition of the rate. All the burnoff profiles are relatively flat in the center and rise sharply on approaching the surface. Work published elsewhere⁶⁰ indicates that the extra near-surface burnoff is indeed real, but that the shapes of the profiles are not consistent with those expected for reaction in the temperature regime of in-pore mass transport control. No differences are evident in the profiles of specimens oxidized in different atmospheres, indicating that no differences in the overall oxidation patterns of differently-treated specimens exist.

Estimates of the diffusion length may be made to ascertain the expected shapes of the oxidant concentration profiles in the specimens. The diffusion length is defined as the distance into the specimen at which the concentration of the oxidant is reduced by 63%, i.e. $C(x=L)/C(x=0) = e^{-1}$. The rate of gasification of a porous material may be limited by the rate of diffusion of the oxidant through its pore network. This may be treated as follows, utilizing a method adapted from the work of Dodson.⁶¹ The observed reaction rate for a presumed first order reaction is given by

$$R_T(\text{sec}^{-1}) = S/V \frac{12P_{ox}}{\rho RT} \eta (D_{eff} K_v)^{1/2}$$

where S/V is the ratio of exposed surface area to volume of the graphite, P_{ox} the partial pressure of oxidant, ρ the graphite density, R the gas constant, T the absolute temperature, η the effectiveness factor, D_{eff} the effective diffusion coefficient of the gas in the graphite and K_v the reactivity of the sample.

Figure 28. Burnoff Profiles of an Axial H451 Graphite Specimen Oxidized in 2% H₂O/He at 850°C to 4.10% Average Burnoff.

Figure 29. Burnoff Profiles of an Axial H451 Graphite Specimen Oxidized in Air to 4.97% Average Burnoff.

Figure 30. "Cocoon" Graphite Specimen. All Components Are H451 Graphite.

Figure 31. Burnoff Profiles of an Axial H451 Graphite Specimen Oxidized in a "Cocoon" in Air at 500°C to 14.14% Average Burnoff.

Figure 32. Local Burnoff Profiles of Three PGX Graphite Specimens Oxidized in Air or 2% H₂O/He.

The diffusion length is defined as $L = (D_{\text{eff}}/K_V)^{1/2}$. In the worst case encountered, L was found to be @ 0.24 cm, so that $L/r_0 \sim 0.25$, where r_0 is the radius of the unoxidized specimen. Here $R_T \sim 1.7 \times 10^{-7} \text{ sec}^{-1}$, $S/V = 2.63 \text{ cm}^{-1}$, $D_{\text{eff}} \sim 0.01 \text{ cm}^2/\text{sec}$ (taken as 1%¹ of the free binary gas diffusion coefficient for $\text{O}_2\text{-N}_2$ ⁶²⁻⁶⁴), $p_{\text{O}_2} = 0.02 \text{ atm}$, $\rho_{\text{H451}} = 1.77 \text{ g/cm}^3$, $T = 833^\circ\text{K}$ and $\eta = I_1(r_0/L) / I_0(r_0/L) \sim 0.79$ (I_1 and I_2 are the modified Bessel functions of the first kind of order 1 and 0, respectively). In the majority of cases, however, the observed reaction rate was sufficiently low that $L/r_0 > 2$, so that the burnoff profiles would be expected to be relatively flat. Although both D_{eff} and K_V generally increase with burnoff, the effect of burnoff on L is not expected to alter this conclusion.

For PGX graphite we calculate L (2% $\text{H}_2\text{O}/\text{He}$, 750°C) = 2 to 8 cm and L (air, 500°C) = 1 to 2 cm, given that R_T is $(0.25 - 1.0) \times 10^{-5} \text{ g/g/min}$ and $(1.5 - 3.5) \times 10^{-6} \text{ g/g/min}$, respectively. Burnoff profiles of similarly oxidized specimens were indeed found to be relatively flat in the center, as exemplified in Figure 32. In the same manner, H451 graphite oxidized in air at 550°C gave rise to the relatively flat burnoff profiles shown in Figures 29 and 31; here the diffusion length was estimated to be $L \sim 1.6$ to 10.6 cm using the measured observed reaction rate of $(0.3 - 2.0) \times 10^{-5} \text{ g/g/min}$.

It is evident then that oxidation in these experiments was rather uniform (reaction occurred primarily in the chemical reaction control regime) and that the dependence on atmosphere of oxidation-induced strength loss must be caused by localized (microstructural) differences which are masked when only bulk properties are examined.

3.2 Strength Loss

The compressive strength of the larger specimens of PGX graphite oxidized in air and in 2% $\text{H}_2\text{O}/\text{He}$ (with or without added H_2) is plotted in Figure 33 as a function of total burnoff. In the case of 2% $\text{H}_2\text{O}/\text{H}_2/\text{He}$, the flow rate of H_2 was set at 120 sccm and that of He at 480 sccm, giving 20% H_2 . It should be noted that some of the specimens shown in this figure were prestressed to 25 to 75% of the mean strength before being oxidized, the results of which are discussed elsewhere.⁶⁵ Similar sets of data are plot-

Figure 33. Compressive Strength of PGX Graphite Oxidized in a 2% H₂O/(20% H₂)/He Mixture at Different Temperatures.

ted in Figure 34 for oxidation of the smaller compressive specimens of PGX graphite in 2% H₂O/He, 2% CO₂/He and 2% O₂/N₂ at various temperatures.

The tensile strength of PGX graphite oxidized in 2% H₂O/He, 2% CO₂/He and 2% O₂/N₂ is shown in Figure 35 as a function of burnoff.

The data obtained for H451 graphite specimens are shown in Figure 36, where the specimens were oxidized either in a 2% H₂O/He mixture or in air, with or without prestress up to 75% of the mean strength. Again, the effect of prestress is dealt with elsewhere.⁶⁵ Loss of tensile strength of H451 graphite oxidized in 2% H₂O/He at a temperature of 835 to 850°C is shown in Figure 37 as a function of burnoff. Figure 38 shows the results of experiments on the effect of oxidation of IG-11 graphite in H₂O-, CO₂-and O₂-containing atmospheres on compressive strength.

Effect of Reaction Temperature on Strength:

In the temperature ranges examined---550-750°C in 2% H₂O/(H₂)/He, 600-850°C in 2% CO₂/He and 400-600°C in 2% O₂/N₂ or in air for PGX graphite; 700-850°C in 2% H₂O/He and 450-600°C in air for H451 graphite; and 750-850°C in 2% H₂O/He and in 2% CO₂/He, and 450-550°C in 2% O₂/N₂ for IG-11 graphite---the strength loss does not appear to depend on the reaction temperature. This is believed to indicate that burnoff of all these specimens occurred in a similar manner. The trend observed here regarding the reaction temperature is in good agreement with the results obtained by Thrower on 2020 and H440 graphites oxidized in air: these graphites showed no significant difference in the amount of loss of compressive strength over the temperature ranges of 500 to 800°C (H440 graphite) and 550 to 700°C (2020 graphite).⁶⁶ Our tensile strength data for H451 graphite oxidized in 2% H₂O/He, though few in number, are comparable to those of Thrower.

The data on IG-11 graphite (Figure 38) indicate that its compressive strength, too, is not affected by the reaction temperature; however, it should be noted that the temperature range examined in this case was only 100 degrees. Data obtained at JAERI for this graphite oxidized in 1.8% H₂O/He at 1,000°C show a strength loss-burnoff trend similar to the result here.⁶⁷

Figure 34. Compressive Strength of PGX Graphite Oxidized in Different Atmospheres as a Function of Total Burnoff.

Figure 35. Tensile Strength of PGX Graphite Oxidized in Different Atmospheres as a Function of Total Burnoff.

Figure 36. Compressive Strength of H451 Graphite Oxidized in Air or in a 2% H₂O/He Mixture at Various Temperatures.

Figure 37. Plots of Tensile Strength Versus Burnoff for H451 Graphite Oxidized in a 2% H₂O/He Mixture at a Temperature of 835 to 850°C.

Figure 38. Compressive Strength of IG-11 Graphite Oxidized in Different Atmospheres as a Function of Total Burnoff.

However, it has been reported that the tensile strength of H451 graphite oxidized in a $\text{H}_2\text{O}/\text{He}$ mixture depends on the reaction temperature, i.e., a lower temperature gives rise to a greater loss of strength (5.2% loss per % burnoff at 800°C) compared with that at a higher temperature (3.6% loss per % burnoff at $1,000^\circ\text{C}$).¹¹ Density profiles of similarly oxidized specimens showed relatively steep burnoff gradients through the specimens oxidized at the higher temperatures.

From the discussion above it appears that oxidation in the present experiments occurred primarily in the bulk burnoff (chemical reaction control) temperature regime, where, as expected, the oxidation temperature did not affect the loss of strength. This is consistent with the burnoff profiles of similarly oxidized specimens, which were presented and discussed in the previous section.

Effect of Oxidizing Atmosphere on Strength:

It can be seen in Figures 33, 34 and 35 that, in the case of PGX graphite, the decrease in both compressive strength and tensile strength due to oxidation at a given total burnoff is greater when the oxidation is carried out in O_2 , i.e., 2% O_2/N_2 or in air, than in $\text{H}_2\text{O}/\text{He}$ or CO_2/He . Since all the specimens are believed to be oxidized primarily in the chemical-reaction control regime and there is no apparent difference in density (or burnoff) profiles between the specimens oxidized in different atmospheres, the substantial enhancement of the strength loss by O_2 at a given burnoff suggests that changes in the microstructure of PGX graphite produced by oxidation in O_2 may be different than the changes created in other atmospheres. Examples of typical scanning electron photomicrographs (SEM) are shown in Figure 39: in photo (b), the surface of a specimen oxidized in 2% $\text{H}_2\text{O}/\text{He}$ at 600°C is seen to have a higher density of pits than that generated by oxidation in 2% O_2/N_2 at 500°C (photo (c)), though the total burnoff of the former specimen was lower than that of the latter (2.77% vs. 5.05%). Some examples of iron x-ray maps (raster scans or XES) and corresponding SEM maps are shown in Figure 40 for PGX graphite oxidized in 2% $\text{H}_2\text{O}/\text{He}$. These maps indicate that oxidation by H_2O was localized around regions rich in iron. No clear correspondence between the distribution of iron and the surface topography was evident for O_2/N_2 oxidation.

(a) Unoxidized

(b) 2% H₂O/He

(c) 2% O₂/N₂

Figure 39. SEM Maps of PGX Graphite Surfaces.

Figure 40. SEM Maps and Iron Raster Scans of an Oxidized PGX Graphite Surface.

The results displayed in Figures 36, 37 and 38 show no significant effect of atmosphere on the compressive strengths of H451 and IG-11 graphites. No topographical differences in the surfaces of specimens oxidized in different atmospheres were observed, either. Iron x-ray maps confirmed the claims of the manufacturers that both of these materials have low iron concentrations (<100 ppm).

The effect of atmosphere on strength loss accompanying oxidation appears to be greatest for PGX graphite, where O_2 -containing atmospheres clearly give rise to a greater loss of strength than CO_2 - or H_2O -containing atmospheres. The burnoff dependence of the strength of H451 graphite oxidized in 2% H_2O/He is almost identical to that for PGX graphite oxidized in 2% CO_2/He and 2% H_2O/He . The burnoff dependence of the strength of IG-11 graphite oxidized in 2% O_2/N_2 , 2% CO_2/He and 2% H_2O/He is similar to these, but not quite the same. The relationship between strength loss and burnoff, or density change, will be discussed later.

The greater strength loss incurred by PGX graphite in O_2 -containing atmospheres compared with H_2O - and CO_2 -containing atmospheres may be attributed to the role of iron in the oxidation reaction. Possible scenarios which focus on the role of iron generally hinge on the distribution and concentration of this impurity, and they implicitly assume that enough H_2 is formed during the reaction to keep the iron catalytically active. In one scenario, the iron is found primarily in the filler particles so that catalytic oxidation in H_2O would occur primarily in the filler particle region, while oxidation in O_2 would occur primarily in the more naturally reactive binder.⁴⁰ Since the binder presumably contributes more than the filler to the strength, at a given burnoff non-catalyzed oxidation would lead to greater loss in strength than iron-catalyzed oxidation. In a second scenario, the iron impurity and the naturally active sites are both uniformly distributed, but the number of iron particles is less than that of the naturally active sites. Oxidation by H_2O leads to formation of large pits in the vicinity of the iron particles, whereas oxidation by O_2 leads to a large number of very small pits. Many small pits may be more effective agents for crack initiation and/or propagation than a few very large ones, either because of their number or because of their geometry.

Finally, a scenario may be described in which the iron impurity is found primarily in the binder but is not distributed uniformly. Oxidation by H_2O (and perhaps CO_2) would lead to formation of large pits in the vicinity of the iron-rich regions, whereas oxidation by O_2 primarily would lead to a large number of very small pits scattered throughout the binder. This may be expected to be the case, particularly at low temperatures where the O_2 oxidation product ratio P_{CO}/P_{CO_2} is quite low; the CO_2 experiments were generally performed at much higher temperatures, where P_{CO}/P_{CO_2} is considerably higher and the opportunity for reductive activation of the iron impurity is greater. As was postulated for the second scenario, the large density of small pits incurred during oxidation in O_2 may be more detrimental to the structural integrity of PGX graphite than the low density of large pits incurred in H_2O or CO_2 .

Inspection of as-received PGX graphite surfaces by optical microscopy (OM), SEM and XES reveals that the impurity iron is not distributed homogeneously at all, but rather is localized in a few regions between grains, i.e., the binder. A typical set of OM/SEM/XES scans is shown in Figure 41. Another set of SEM/XES scans is shown in Figure 42. Thus, the first two scenarios described above can be eliminated as possible mechanisms for the oxidation of PGX graphite. The third scenario appears to be the most attractive. However, other properties of PGX graphite which have not yet been examined could be responsible for the phenomenon.

The compressive strength of oxidized graphite containing large levels of iron, vanadium and calcium was recently measured.^{16,68} The Fe-doped specimens were impregnated by adding Fe_2O_3 to the binder before the molding stage, while the V- and Ca-doped specimens were impregnated by adding the metals to the pitch used for manufacturing the coke. The results indicated that, at any given burnoff, strength loss followed the trend $Ca > V > Fe$. Further, oxidation of the iron-doped specimens in H_2O had to proceed to ~20% burnoff for the compressive strength to reach 50% of its ultimate fracture strength, while in CO_2 or air a burnoff of 15% was necessary to achieve that same strength loss. Generalization of the results of these workers is quite difficult. In the first place, the graphites used in their study appeared to be quite variable, e.g., the iron concentration of their high-iron graphite ranged from 10

OM X300

SEM X300

OM X1000

SEM X1000

FE X-RAY SCAN X1000

Figure 41. Optical (OM) and Electron (SEM) Photomicrographs of the Polished Surface of an Unoxidized PGX Graphite Specimen.

Figure 42. Surface Maps of Unoxidized PGX Graphite.

(a)	SEM, 500X	(c)	SEM, 1800X
(b)	Iron X-Ray Scan, 500X	(d)	Iron X-Ray Scan, 1800X

to 1,000 ppm and the densities of the specimens varied from 1.71 to 1.82 g/cm³. Secondly, the location of the impurities, their chemical form, their concentrations and the nature of the graphites themselves are all quite different for these specimens as compared to PGX graphite. For instance, a glance at Table II reveals that the abundances of V and Ca in PGX are much lower than that of Fe. Certainly the effects of impurities on oxidation-induced strength loss need to be investigated further.

Mention should be made of the work of Zimmer⁶⁹, wherein the effects of oxidation of PGX graphite on its fracture mechanism was examined. The fracture path (after failure under compression) for material oxidized in either air or H₂O appeared to follow the preferentially oxidized binder between grains, but no clues about the initiation of the dominant crack were unearthed. Additional information about the effects of oxidizing environment on the initiation and propagation of stress-induced cracks is needed to solve the PGX graphite riddle.

Relationship of Strength to Burnoff:

The effect of burnoff on strength of graphite has often been expressed by an equation of the form^{4,5,6}

$$\frac{S}{S_0} = \alpha \left(\frac{\rho}{\rho_0} \right)^\beta, \quad (1)$$

where S is the strength of the material at fractional burnoff, B ; S_0 is the mean strength of the unoxidized material; and ρ/ρ_0 is the ratio of the bulk density at burnoff, B , to that before treatment, i.e., $\rho/\rho_0 = 1 - B$, provided that oxidation has caused no dimensional changes, which was practically the case for the specimens examined here. The coefficient α is usually set equal to 1 and β is another constant. The results for PGX graphite oxidized in 2% O₂/N₂ at 500°C and in air at 450 to 550°C are displayed as a logarithmic plot of the above expression in Figure 43. A single straight line through the origin with a slope of 10.6 (β) appears to fit both sets of data quite well. The results for PGX graphite oxidized in various environments are summarized in Figure 44. The results for oxidation in 2% CO₂/He and 2% H₂O/He were fitted with expressions of the form above to yield $\beta = 7.53$ and $\beta = 6.8$, respectively. However, the fits for these two cases are quite poor, especially at low burnoffs.

Figure 43. Relationship Between Loss of Compressive Strength and Density Change for PGX Graphite Oxidized in 2% O₂/N₂ or in Air.

Figure 44. Relationship Between Loss of Compressive Strength and Density Change for PGX Graphite Oxidized in Various Atmospheres.

The results for IG-11 graphite oxidized in 2% O₂/N₂, 2% H₂O/He and 2% CO₂/He are plotted in Figure 45 in similar fashion to the PGX data. The H₂O oxidation data were fitted to the relation

$$\frac{S}{S_0} = \left(\frac{\rho}{\rho_0}\right)^{7.13}$$

while the O₂ oxidation data were fitted to

$$\frac{S}{S_0} = \left(\frac{\rho}{\rho_0}\right)^{6.08}$$

The scatter in these two sets of data is sufficiently high to warrant considering them as one set of data. The large scatter and paucity of the CO₂ data preclude fitting an expression to them, but it can be seen that they fall in the vicinity of the H₂O and O₂ results.

Although the deviation is rather large at low burnoffs, Equation (1) can, nevertheless, be fitted to the data for PGX and IG-11. However, for H451 graphite, Equation (1) cannot be fitted at all, as is shown in Figure 46.

The strength loss incurred by graphite during gasification is directly related to the type and amount of material removed. Removal of material is generally manifested as development of porosity. However, gasification of graphite generally does not lead to uniform development of its pore network, since the virgin material itself has a rather broad multi-modal distribution of pore sizes: the pore structure consists of an interconnected array of ultra-micropores and micropores (with radii given by $r < 1 \times 10^{-3} \mu\text{m}$), mesopores ($1 \times 10^{-3} < r < 2.5 \times 10^{-3} \mu\text{m}$) and macropores ($r > 2.5 \times 10^{-3} \mu\text{m}$). It is well known that during the initial stages of oxidation, micro/mesopores, as well as closed pores, open up, while macropores greater than $1 \mu\text{m}$ are little affected; during later stages of the oxidation, development of the macropores becomes important.²⁹

One may view the pore development process, at least during the first stages of oxidation, as the development of two independent pore networks. The effects of burnoff in the two networks may be treated separately so that the strength-burnoff relationship can be given by

$$\frac{S}{S_0} = \alpha \left(\frac{\rho}{\rho_0}\right)^\beta + \gamma \left(\frac{\rho}{\rho_0}\right)^\delta . \quad (2)$$

Figure 45. Relationship Between Loss of Compressive Strength and Density Change for IG-11 Graphite Oxidized in Different Atmospheres.

Figure 46. Plots of Loss of Compressive Strength and Density Change for H451 Graphite Oxidized in 2% H₂O/He or in Air.

Equation (2) is simplified by noting that $\alpha + \gamma = 1$, since $S = S_0$ when $\rho = \rho_0$. Values of α and β can be estimated at the limit of $\rho/\rho_0 \rightarrow 0$, i.e.,

$$\lim_{\rho/\rho_0 \rightarrow 0} \frac{S}{S_0} = \alpha \left(\frac{\rho}{\rho_0} \right)^\beta \quad (3)$$

As illustrated in Figure 46, the data for H451 graphite are well expressed over the entire burnoff range examined in the present experiment by the relationship

$$\frac{S}{S_0} = 0.79 \left(\frac{\rho}{\rho_0} \right)^{3.5} + 0.21 \left(\frac{\rho}{\rho_0} \right)^{71.5} \quad (4)$$

Fitted values of α , β , and δ were also estimated for the other graphites; these are displayed in Table V. Some examples of the fitted curves are shown in Figures 47-50.

It is believed that the second term of the right-hand side of Equation (2) corresponds to development of the micro/mesopores of the graphite matrix, a process which dominates the oxidation at low burnoffs but contributes very little at high burnoffs. It is interesting that the ratio δ/β is relatively independent of both the material and the oxidizing gas; the value $\delta/\beta \sim 10-20$ also corresponds to the expected ratio of active surface area in the micro-/mesopores to that in the macropores. The relatively small value of α in the case of tensile strength loss may be interpreted, in this scheme, to greater contribution of small flaws to fracture in the tensile mode.

Experiments designed to yield information about the effects of in-pore diffusion and pore development on the structural integrity of graphite are currently underway. The results they yield, together with more extensive reactivity/strength loss data for IG-11, H451, PGX and several other HTGR candidate graphites will be presented in Part II of this report.

4. CONCLUSIONS

The effects of oxidizing atmosphere and temperature on the reactivities and strengths of PGX, H451 and IG-11 graphites have been examined. Optical microscopic and scanning electron microscopic observations have also been carried out for these graphites oxidized in various atmospheres.

Figure 47. Relationship Between Compressive Strength Loss and Density Changes for PGX Graphite Oxidized in 2% H₂O/He (solid circles) and 2% CO₂/He (triangles).

Figure 48. Relationship Between Tensile Strength Loss and Density Change for PGX Graphite Oxidized in 2% O₂/N₂.

Figure 49. Relationship Between Tensile Strength Loss and Density Change for PGX Graphite Oxidized in 2% H₂O/He (solid circles) and in 2% CO₂/He (triangles).

Figure 50. Relationship Between Compressive Strength Loss and Density Change for IG-11 Graphite Oxidized in 2% O₂/N₂ and 2% H₂O/He.

Table V.

Fitted Values of α , β and δ in the Equation

$$\frac{S}{S_0} = \alpha \left(\frac{\rho}{\rho_0} \right)^\beta + (1-\alpha) \left(\frac{\rho}{\rho_0} \right)^\delta$$

Graphite	Atmosphere	Stress Mode	α	β	δ
PGX	Air, O ₂	C	0.94	9.4	194
PGX	H ₂ O, CO ₂	T	0.86	10	100
H451	Air, H ₂ O, CO ₂	C	0.79	3.5	71.5
	H ₂ O	T	0.62	3.5	30
IG-11	H ₂ O, O ₂ , CO ₂	C	0.83	4.0	40

† C= compression, T = Tension

Preliminary measurements of the oxidation kinetics of these graphites in H_2O -, CO_2 - and O_2 -containing atmospheres were made. Some anomalous effects of flow rate and burnoff were observed, particularly with PGX graphite. These were explained by invoking a surface burnoff phenomenon or a mechanism based on the roles of impurities. Reactivity of PGX graphite was found to vary linearly with $[Fe]$, and in the case of oxidation in H_2O/He mixtures, with $[H_2O]$. The reactivity of PGX graphite toward $H_2O/H_2/He$ mixtures showed a large amount of variability (factor of X50), even after normalization to the same $[Fe]$. Reactivities in H_2O or O_2 followed the trend $R(PGX) > R(H451) > R(IG-11)$; in H_2O/H_2 the gap between PGX and the other two graphites widened considerably. Activation energies for oxidation in CO_2 , H_2O and O_2 were estimated, too, generally giving rise to $E_a(O_2) < E_a(H_2O) < E_a(CO_2)$, as expected.

The loss of compressive and tensile strength incurred by PGX graphite after oxidation in 2% O_2/N_2 was almost identical to that lost in air, but this was significantly greater than the loss of strength incurred in 2% H_2O/He and 2% CO_2/He . The results for 2% H_2O/He and 2% CO_2/He were similar to those obtained for H451 graphite oxidized in air and 2% H_2O/He , and IG-11 graphite oxidized in 2% O_2/N_2 , 2% H_2O/He and 2% CO_2/He . The anomalous behavior of PGX graphite may be attributed to its iron impurity, which is distributed unevenly as mobile clusters in some regions of the binder. Oxidation of PGX graphite in 2% H_2O/He or CO_2/He is probably localized around the iron impurity, leading to formation of large pits; oxidation in O_2 -containing environments occurs more uniformly and produces a high density of small pits, which may be more detrimental to the graphite's structural integrity.

The dependence of strength on burnoff was found to be independent of oxidation temperature in the chemical reaction control regime. However, attempts to fit the strength-burnoff data to the often-used expression,

$$\frac{S}{S_0} = \alpha \left(\frac{\rho}{\rho_0} \right)^\beta$$

were not completely successful; in most cases, specimens appeared to behave differently at low burnoffs than at high burnoffs. Here, S , S_0 , ρ and ρ_0 are the strength of the oxidized specimen, the mean fracture strength of the untreated material, the bulk density after oxidation and the density before oxidation, respectively; α and β are constants.

The data are represented better by the proposed equation,

$$\frac{S}{S_0} = \alpha \left(\frac{\rho}{\rho_0} \right)^\beta + (1-\alpha) \left(\frac{\rho}{\rho_0} \right)^\delta ,$$

where δ is a constant. It is believed that the first and second terms of the right-hand side of this expression correspond to oxidation in the macropores and in the micro/mesopores, respectively. The ratio δ/β was found to be relatively constant, ranging from 10 to 20, while the value of α for all the specimens examined was 0.8 to 0.9 for compression and about 0.6 for tension.

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