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**High-Temperature Oxidation
of Graphite Rods with
Temperature Control by
Combustion Gas Recycle**

Ronald M. Canon

OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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HIGH-TEMPERATURE OXIDATION OF GRAPHITE RODS WITH
TEMPERATURE CONTROL BY COMBUSTION GAS RECYCLE

Ronald M. Canon

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HIGH-TEMPERATURE OXIDATION OF GRAPHITE RODS WITH TEMPERATURE CONTROL BY COMBUSTION GAS RECYCLE

Ronald M. Canon

ABSTRACT

The combustion of graphite (fuel blocks) is of fundamental importance in the fuel reprocessing scheme for the High-Temperature Gas-Cooled Reactor (HTGR). A study was made to evaluate a chunk-type burner for possible application in this reprocessing step. The combustion gases were recycled to allow operation at higher burn rates without an increase in graphite temperature. Graphite rods of two diameters were oxidized with makeup oxygen and recycled stack gases at various gas flow rates in an insulated reactor. Results of this study indicate a strong dependence of oxygen transfer on gas flow rate with little effect resulting from changes in graphite temperature. High carbon monoxide concentrations in the exit gas were not a problem except at oxygen concentrations below ~5%. Stable operation of a recycle controlled burner was achieved, avoiding the temperature excursions common in previous graphite burners.

1. INTRODUCTION

Oxidation of carbon and graphite has been studied for a variety of reasons. Tu et al.¹ investigated the combustion rates of carbon spheres (2.5 cm in diam) in air at low velocities. Kuchta et al.² burned carbon cylinders (0.37 cm in diam and 3.0 cm in length). However, a survey of the literature indicates that very little work has been done on the burning of large graphite chunks. This area is of special interest primarily because of the graphite oxidation step in the reprocessing of fuel elements from the High-Temperature Gas-Cooled Reactor (HTGR). In the whole-block burner approach to this problem, intact fuel elements would be loaded into a reactor and burned with oxygen. A number of

problems are presented by such a system. The fuel kernels are distributed in the graphite matrix and can be damaged by excessive temperature--the upper limit being $\sim 1600^{\circ}\text{C}$. The carbon monoxide concentration in the gas phase must also be adequately controlled to maintain safe operations.

In order to gain an understanding of the graphite oxidation process, a number of experiments have been performed with an insulated reactor, and the data have been analyzed. The results of the analysis are applicable to any gas-solid reactor operating adiabatically (i.e., without wall heat transfer).

2. EXPERIMENTAL

2.1 Principles of Operation

The major gas-solid chemical reactions that occur in solid graphite rods during combustion are:

In addition to these, a gas-phase reaction occurs:

Reactions (1) and (2) are very rapid, and at temperatures above 900°C , the rate of combustion is controlled by the availability of oxygen. Both of these reactions are exothermic; therefore, the process is

self-sustaining after the ignition temperature is reached. A large amount of heat is supplied which is only partially utilized by reaction (3).

The rate of reaction (3) as reported by Haas³ is primarily determined by the graphite surface temperature and can be expressed by the following equation:

$$R_1 = 5.0 \times 10^3 \exp (-24000/T_s) . \quad (5)$$

This reaction rate is very low below 1200°C and of little importance in relation to the rates of reactions (1) and (2) for this system. Although carbon monoxide production by reaction (2) is highly favored for all temperatures studied, carbon monoxide is quickly oxidized by reaction (4) because it counterdiffuses with oxygen in the gas boundary layer. As a result, significant levels of carbon monoxide flue gas are not encountered unless the oxygen content is near zero. Extremely high burning temperatures (above 1450°C) would probably result in high carbon monoxide gas concentrations due to a rate increase in reaction (3) and a decrease in available oxygen by reaction (4). The generated heat is removed by convective transport to the combustion gases. The mass flow of gas is kept at a level sufficient to maintain the graphite temperature below 1200°C.

2.2 Apparatus

The reactor or burner used in this work (see Fig. 1) is a 14-in. pipe, ~58 in. long, and is fabricated from type 347 stainless steel. The upper section, 35 in. long, contains the burning zone and is externally insulated. The firebrick liner and insulation prevent high wall temperatures and reduce the heat losses to ~5%. The cooling coils are fabricated

Fig. 1. Graphite burning vessel.

from stainless steel tubing and arranged in a multiple spiral configuration. The graphite support is firebrick and rests on a water-cooled pipe. Initial heating of the reactor is accomplished with two clamshell heaters, each having an ID of 4.5 cm.

The burner wall temperature is measured by 12 thermocouples, and six thermocouples are used to measure the gas temperature. The graphite used in this study is type H-327 (analysis shown in Table 1) fabricated into solid rods measuring 2.6 or 3.8 cm in diam and 56 cm in length and drilled to accept five 1/16-in.-diam thermocouples. Four thermocouples are placed axially into the rod to depths of 2.5, 15.2, 30.5, and 45.7 cm and are 0.6 cm from the outside of the rod. The fifth thermocouple is inserted to a depth of 45.7 cm on the rod axis. The gas temperature between the burning and cooling sections is utilized in a control loop to maintain constant exit-gas temperature by manipulation of the recycle rate. Figure 2 shows the entire burning facility. The equipment is located within a walk-in hood to ensure proper ventilation for off-gas removal. Any carbon particles entrained in the flue gas are removed by a cyclone separator and sintered-metal filter. A gas-gas heat exchanger preheats the recycle gas, and a water-cooled exchanger is employed to reduce the temperature of the flue gas to 40 to 60°C. Hot flue gases are on the tube side in both exchangers. A rotary blower, equipped with a bypass control loop, pressurizes the gases for recycle. All gas flow rates are measured with rotameters, and the off-gas is continuously analyzed for oxygen, carbon monoxide, and carbon dioxide. Carbon monoxide and carbon dioxide concentrations are measured with infrared absorption analyzers; a paramagnetic analyzer detects the oxygen.

Table 1. Typical impurities in graphite
determined by spectrographic analysis

Component	Wt ppm
Al	<10
Cd	<25
Co	<25
Fe	10
Nb	<50
Pb	<10
Si	10
Sr	<200
Th	<50
W	<50
Zn	<50

Fig. 2. Schematic diagram of adiabatic graphite oxidation equipment.

3. RESULTS

3.1 Experimental

Oxygen concentration and gas flow rate are the major variables affecting burn rate and temperature. By operating at the upper limit (for this equipment) of gas flow and with 30% oxygen feed, graphite burn rates of $0.030 \text{ g/cm}^2\text{-min}$ have been obtained. However, oxygen utilization at such high burn rates is relatively poor (74%). At lower burn rates ($0.02 \text{ g/cm}^2\text{-min}$), oxygen utilizations as high as 90% (requiring only 11% excess oxygen) have been achieved. Inlet gas temperatures ranged from 30 to 225°C , while exit temperatures were 600 to 1100°C . Temperature increases up to 1000°C were achieved across the reactor. As indicated in Fig. 3, the gas flow rate has a major effect on burning rate; however, there has been no apparent relationship between burn rate and temperature. The rod is always coolest at the leading end because of lower gas temperatures at the inlet. This is true even in the cases of higher burn rates at the leading edge, as indicated in Fig. 4.

Carbon monoxide concentrations were low for all the experiments and never approached the explosive concentration of 12.5%. However, when high (>90%) oxygen utilization was achieved, the steady-state carbon monoxide content increased to as much as 4%. The presence of oxygen inhibits the accumulation of carbon monoxide due to gas-phase oxidation (reaction 4).

Carbon dioxide and carbon monoxide concentrations were integrated with gas flow to provide a material balance on carbon. By comparison with the remains of the graphite rod, the balance was found to close

Fig. 3. Graphite weight loss as a function of gas flow rate.

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Fig. 4. Effect of position on burning rate and temperature.

with an average error of 7% and was generally better for high gas flow rates.

Figures 5 and 6 show the transient behavior of the adiabatic graphite burner. The carbon monoxide concentration changes very little after the initial spike. The maximum initial carbon monoxide content encountered for any run was 10%. A steady-state temperature is also reached fairly quickly. In most of the experiments, the reactor was shut down when approximately one-half of the rod had been burned. In order to maintain a simple cylindrical geometry, data analysis was applied only to the initial graphite oxidation (20% burnup of the rod).

3.2 Analysis of Data

For instantaneous gas-solid reactions, the relation

$$\frac{BR}{X_{O_2}} = k_g^* \tilde{\rho} \quad (6)$$

can be used to adjust the burning rate (BR) for varying oxygen concentration (X_{O_2}). The average mass-transfer coefficient, k_g^* (cm/s), can then be calculated from the gas molar density, $\tilde{\rho}$ (g-mol/cm³), and the burn rate. Mass-transfer data are plotted in Fig. 7 as a function of the product of the logarithmic mean Reynolds and Schmidt numbers. The Reynolds number for the annular cross section is

$$N_{Re} = \frac{4W}{\pi \mu (D_o + D_i)} \quad (7)$$

The Schmidt number is

$$N_{Sc} = \frac{\mu}{\rho D} \quad (8)$$

Fig. 5. Burner exit gas composition as a function of time.

Fig. 6. Graphite temperatures as a function of time.

Fig. 7. Effect of mass-transfer Peclet number on oxygen transfer.

The Reynolds-Schmidt product is only a function of mass flow, density, diffusivity, and the diameters of both the rod and the reactor. With the dimensions fixed, this product is a function only of mass flow, temperature, and pressure. Often called the Peclet number for mass transfer (N_{Pe}), this product can be used to correlate the burning data. Laminar data for graphite burning are shown on the left side of Fig. 7 and are best represented by

$$k_g^* \bar{\rho} = (8.20 \pm 5.80) \times 10^{-9} (N_{Pe})_{LM}^{1.40 \pm 0.35} \quad (9)$$

The dashed lines indicate the 95% confidence range. The turbulent and transition data are shown on the right side of Fig. 7 and are best represented by

$$k_g^* \bar{\rho} = (1.54 \pm 0.10) \times 10^{-5} (N_{Pe})_{LM}^{0.26 \pm 0.07} \quad (10)$$

The constants in Eqs. (9) and (10) have units of $\text{g-mol cm}^{-2} \text{sec}^{-1}$. The correlation coefficients for the laminar and turbulent data are 0.97 and 0.93 respectively.

For the diffusion controlled reaction, the burn rate is equal to the rate of diffusion which can be expressed as

$$BR = \frac{2 X_{O_2} D P}{D_i RT \ln (2\delta/D_i + 1)} \quad (11)$$

or on rearranging to solve for the film thickness,

$$\delta = \frac{D_i}{2} \left\{ \exp \left[\frac{2DP}{D_i RT (BR/X_{O_2})} \right] - 1 \right\} \quad (12)$$

As indicated by Slattery and Bird,⁴ the diffusivity of oxygen at these temperatures may be expressed as

$$D = 4.77 \times 10^{-6} T^{1.823} \quad (13)$$

Since the pressure for all runs was approximately the same, Eqs. (12) and (13) can be combined to give

$$\delta = \frac{D_i}{2} \left\{ \exp \left[\frac{1.16 \times 10^{-7} T^{0.823}}{D_i (BR/X_{O_2})} \right] - 1 \right\} \quad (14)$$

Film thicknesses calculated from Eq. (14) are shown in Fig. 8. The data in Figs. 7 and 8 indicate that a transition is occurring for this system at a Peclet number of 1000.

4. CONCLUSIONS

The reaction of nuclear-grade graphite with oxygen in an insulated reactor with flue-gas recycle can be described by diffusion considerations at graphite temperatures of <1200°C. The experimental data can be correlated with the mass-transfer Peclet number. Laminar data show a strong dependence on gas-stream velocity ($N_{pe} \propto V$) that is consistent with diffusion control. Turbulent data show some velocity dependence but of a much weaker nature. Temperature excursions do not occur with the flue-gas recycle system. Manual flow adjustment can be used to maintain desired burning temperatures, or a simple gas recycle system can be controlled by the temperature of the exit gas. Some oscillation can be expected to occur because of the heat capacity of the burner and its contents, but

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Fig. 8. Effect of Peclet number on film thickness.

they are minor in magnitude (oscillations of 75°C were noted). Additionally, the following observations were made:

1. There is no apparent dependence of reaction rate on graphite temperature for the conditions studied (1000 to 1200°C).
2. An increase in oxygen concentration of the inlet-gas stream (and a consequent reduction in carbon dioxide) results in an increase in the burning rate. This increase in burning rate is accompanied by an increase in surface temperature simply because heat generation has been increased without enhancement of heat removal. The temperature rise is, therefore, a result of (rather than a cause for) the increased reaction rate.
3. A burner exit oxygen concentration of 5% is sufficient to prevent high levels of carbon monoxide in the reactor.
4. Oxygen utilizations $>90\%$ can be obtained with the recycle reactor with a burning zone length of 56 cm. Longer zone lengths would result in increased utilization but also higher levels of carbon monoxide.
5. Operation of the burner with no excess air probably will result in unacceptable (above the explosive limit) concentrations of carbon monoxide.

Nomenclature

- BR = carbon burning rate, $\text{g-mol/cm}^2 \text{ s}$
 D = diffusivity of O_2 in CO_2 , cm^2/s
 D_i = graphite rod diameter, cm
 D_o = inside diameter of reactor, cm
 k_g^* = gas-phase mass-transfer coefficient, cm/s
 M = average molecular weight of gas, g/g-mol
 N_{Pe} = mass-transfer Peclet number, $N_{Re} N_{Sc}$, dimensionless
 N_{Re} = annular Reynolds number, dimensionless
 N_{Sc} = Schmidt number, dimensionless
 P = burner gas pressure, atm
 R = universal gas constant, $\text{cm}^3 \text{atm/g-mol } ^\circ\text{K}$
 R_1 = carbon reacted, $\text{g-mol/cm}^2 \text{ min}$
 T = average of gas and surface temperatures, $^\circ\text{K}$
 T_s = surface temperature, $^\circ\text{K}$
 W = gas mass flow rate in reactor, g/s
 X_{O_2} = bulk stream oxygen mole fraction, dimensionless

Greek Letters

- δ = gas film thickness, cm
 μ = gas mixture viscosity, g/cm s
 ρ = gas density, $M\rho$, g/cm^3
 $\tilde{\rho}$ = molar gas density, g-mol/cm^3

Subscript

- LM = logarithmic mean value over reactor length

5. ACKNOWLEDGMENTS

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