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INTRODUCTION

High-purity, nuclear-grade graphites react very slowly with oxygen and are noncombustible by conventional standards. Nevertheless, graphite combustibility has always been a subject of discussion for graphite-moderated nuclear reactors, primarily because of the accidents at Windscale in 1957 [1] and Chernobyl in 1986 [2]. An assessment of the Windscale accident concluded oxidation occurred primarily with the metallic uranium fuel [1]. An analysis of the Chernobyl accident [3] showed any convective airflow into the damaged core would provide a net cooling effect, i.e., heat removed by convection was predicted to be greater than heat generated by the exothermic reaction of graphite with oxygen, and the dominant heat source causing the "red glow" was the result of nuclear-decay processes.

One definition for graphite combustion is rapid oxidation at high temperatures. Burning may be defined as self-sustained combustion, such that high temperatures are maintained by the combustion process itself, i.e., the combustion heat-generation rate matches or exceeds the rate of heat loss by conduction, convection, and radiation. For burning to occur, several conditions must exist simultaneously: (i) an appropriate geometry with high surface-to-volume ratio; (ii) sufficiently high temperatures; (iii) adequate oxygen supply; (iv) a high intrinsic reaction rate; and (v) a favorable heat balance with small heat losses. These conditions are very difficult to satisfy for high-purity, nuclear-grade graphites.

GRAPHITE OXIDATION THEORY

For a lumped mass of graphite, the energy-conservation equation is given by

$$\overline{m_G C_{p,G}} \frac{dT_G}{dt} = \dot{m}_C \Delta Q + q_{\text{loss}} \quad (1)$$

where $\overline{m_G C_{p,G}}$ is the effective heat capacity of the graphite, T_G is the graphite temperature, \dot{m}_C is the carbon mass-loss rate caused by the graphite-oxygen reaction, ΔQ is the heat released per unit mass of carbon reacted, and q_{loss} is the heat-loss rate by conduction, convection, and radiation. The quantity ΔQ will depend on the reaction-product mixture of CO and CO₂, which

depends on temperature. At lower temperatures more CO₂ is formed, whereas at higher temperatures CO is the dominant reaction product [4]. The carbon mass-loss rate is determined by solving the species-conservation equation for O₂ within the graphite pores, subject to a convective boundary condition at the gas/graphite interface. For a slab geometry, the O₂ species-conservation equation is given by

$$\frac{d^2 Y_{O_2}}{dx^2} = \delta \xi_{O_2} Y_{O_2}^n \quad (2)$$

where Y_{O_2} is the pore-volume-averaged mass fraction of O₂. The parameters δ and ξ_{O_2} are defined according to

$$\delta = \frac{F_c F_b k}{\phi D_{O_2} Y_{O_2}^n} \quad (3)$$

$$\xi_{O_2} = (1 - f_{CO}/2) \frac{W_{O_2} \rho_G}{W_C \epsilon \rho} \quad (4)$$

where F_c is a catalysis factor to account for possible enhancement of the chemical reactivity by impurities, F_b is a burnoff factor to account for the effect on chemical reactivity resulting from the evolution of the internal pore structure caused by burnoff, k is the graphite intrinsic reaction rate (in the units mass/mass-time) at zero burnoff for kinetically-controlled oxidation, ϕ is the tortuosity coefficient for diffusion in graphite ($\cong 0.01$ at zero burnoff), D_{O_2} is the binary diffusion coefficient for oxygen in nitrogen, f_{CO} is the number of moles of CO formed per mole of C reacted, W_K is the molecular weight of species K, ρ_G is the graphite density ($\cong 1.7$ g/cm³ at zero burnoff), ϵ is the graphite void fraction ($\cong 0.2$ at zero burnoff), and ρ is the density of the gas mixture. In Eq. (2) it is assumed that the intrinsic reaction rate k is of the form

$$k = A_0 \exp(-T_A/T_G) p_{O_2}^n \quad (5)$$

where A_0 is a pre-exponential constant, T_A is the activation temperature, p_{O_2} is the oxygen partial pressure, and n is the order of reaction with respect to p_{O_2} . The intrinsic rate measurements for most graphites indicate

$n \cong 0.5$. Since $p_{O_2} \propto Y_{O_2}$, the quantity δ is independent of Y_{O_2} . Analyses are performed by treating the graphite as a series of thermally-connected masses and modeling heat and mass transfer with chemical reactions in a flow channel that is coupled to the graphite using convective boundary conditions. Predictions using models of this type have shown good agreement with previous data for oxidation of nuclear-grade graphite [5].

RECENT EXPERIMENTS

Representative tests for assessing combustibility of nuclear-grade graphite were performed recently at Los Alamos National Laboratory (LANL). The test specimens consisted of annular H-451 graphite tubes that simulated the geometry associated with a single coolant hole of a Modular Helium Reactor (MHR) fuel element. The tube dimensions were as follows: inner diameter = 1.6 cm, outer diameter = 3.4 cm, and length = 80 cm. The specimens were heated in a three-zone furnace which was insulated to minimize heat losses. An oxygen/nitrogen mixture was preheated to near the graphite temperature and introduced into the annular region of the test specimen. Thermocouples were used to measure graphite temperatures along the length of the specimen. The concentrations of O_2 , CO , and CO_2 in the effluent gas were measured also. Two tests were completed for initial graphite temperatures of $\sim 500^\circ C$ and $\sim 700^\circ C$, respectively. The mass-flow rate of 0.015 g/s was selected to be representative of a buoyancy-driven flow and the inlet O_2 mole fraction of 0.1 was judged to be representative of hypothetical MHR accident scenarios, in which some oxygen depletion would occur before the airflow entered the reactor core.

For the $500^\circ C$ test, very little oxidation occurred and the graphite temperature remained near $500^\circ C$ throughout the test (primarily because of the furnace heaters). Figure 1 shows the graphite temperature response for the $700^\circ C$ test. The maximum temperature increase after 6.5 hr of oxidation was only $\sim 25^\circ C$ and occurred at an axial location ~ 25 cm from the tube inlet. The total graphite burnoff was $\sim 1.1\%$. Measurements of the surface burnoff indicated oxidation was occurring in the in-pore, diffusion-controlled regime. Measurements of the exit gas concentration showed nearly all of the O_2 was converted to CO_2 . This result indicated CO deflagration occurred in the flow channel, since the dominant graphite/oxygen reaction product at $700^\circ C$ should be CO [4]. However, CO deflagration had apparently little effect on the graphite temperature response and the overall oxidation behavior.

Because the boundary conditions associated with the furnace assembly were difficult to characterize, it was not

possible to predict the small changes in graphite temperature with good accuracy. Consequently, the measured graphite temperatures were used as prescribed boundary conditions, and the oxidation behavior and effluent gas compositions were predicted with reasonable accuracy.

CONCLUSIONS

Graphite oxidation involves complex phenomena and can be difficult to predict if boundary conditions are not accurately known. The graphite temperature response is limited by the graphite heat capacity, a low intrinsic reaction rate, mass-transfer effects that further limit the reaction rate, and heat losses to the surroundings. The recent LANL data confirm these limitations and show nuclear-grade graphites oxidize at much slower rates than charcoal, coal, and other less pure and more porous forms of carbon. Hypothetical MHR accidents that allow air ingress into the graphite core would require large-scale failure of the steel reactor vessel and would be classified as beyond design-basis events. Even if such an accident did occur, the airflow would likely have little effect on the graphite temperature response.

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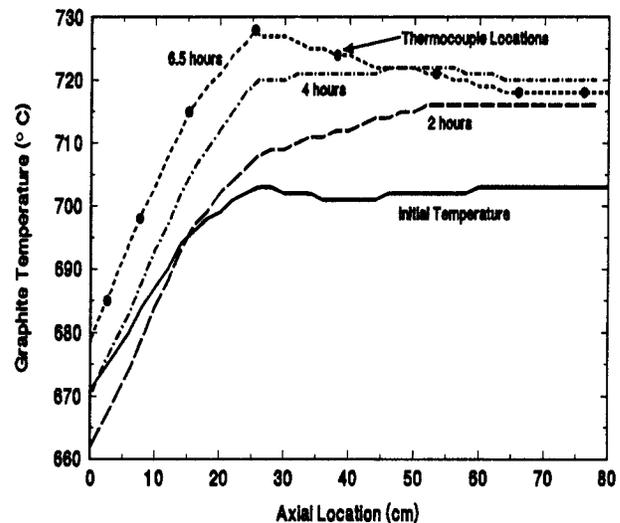


Fig. 1. Graphite temperature response during LANL test.