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SUMMARY REPORT
HANFORD STUDIES
OF EGCR COMBUSTION CHARACTERISTICS

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by

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October 10, 1961

Nonmetallic Materials Development Operation
Hanford Laboratories Operation
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SUMMARY REPORTHANFORD STUDIES OF EGCR COMBUSTION CHARACTERISTICSINTRODUCTION

The reaction of oxygen with graphite is exothermic. If, due to some accident, massive amounts of air were drawn into contact with hot moderator graphite in the EGCR, it is conceivable that the heat generated from the oxidation, added to the after-heat of the reactor, might exceed the cooling capabilities of a damaged coolant system. In this event, the temperature of the moderator would continue to rise even though the reactor was shut down. Depending on circumstances, the rate of temperature rise might be quite slow, giving ample time to correct the situation, or might be very rapid.

The exact conditions under which self-sustained combustion can occur, i.e., when the heat generated equals or exceeds the heat removed by the coolant, depends strongly on the geometry of the moderator system, the initial heat distribution, and the coolant flow. The geometry determines the amount of graphite which is exposed to oxygen and can be involved in the combustion process. The consideration of geometry is complicated by the fact that not only the surface of the graphite oxidizes, but, because of the porous nature of graphite, the oxidation extends to some depth below the surface. The temperature distribution of the reactor determines which regions of graphite are capable of undergoing self-sustained combustion. The temperature distribution includes considerations of both coolant and graphite temperature as well as the rate of heat decay after shutdown. The coolant flow controls the rate at which heat can be removed from the system and at the same time, if there is air mixed with the coolant, determines the rate of access of oxygen to the hot graphite surfaces.

Aside from the system variables just mentioned, there are other significant factors which affect the rate at which graphite will oxidize. These are: the type of graphite, that is structure and impurity level in the graphite; the presence of impurities which have been deposited on the graphite; the irradiation history of the graphite; the amount of prior oxidation which the graphite has undergone; the intensity of gamma radiation; the presence of moisture; and the partial pressure of oxygen in the coolant.

Because of the large number of interrelated variables which affect the possibility of establishing a self-sustained combustion condition within the reactor, the Hanford studies to evaluate the problem have been conducted in several parts. In the first phase of the work, the temperature, geometry and flow conditions which exist in the EGCR have been duplicated as closely as possible in an engineering scale mock-up. This mock-up is designated

the "EGCR Burning Rig". Other variables which could not be incorporated readily in the Burning Rig tests, such as the effect of gamma radiation, have been investigated in separate laboratory experiments. Results of the Burning Rig tests have been used along with appropriate correction factors devised from the laboratory studies as basis for predicting the combustion characteristics of the EGCR. The final prediction as to whether self-sustained combustion can exist in EGCR is made on an electronic computer; the computer work has been done at Allis-Chalmers and at Oak Ridge National Laboratory. The accuracy of the computer code has been checked by testing the ability of the machine computation to predict the combustion characteristics of the EGCR Burning Rig. With the code appropriately adjusted to accomplish this task, confidence has been increased in the capability of the computation to predict reactor behavior.

The final phase of the Hanford work has been devoted to evaluating means for limiting the possibility or seriousness of combustion occurring in the EGCR. Part of this study has been concerned with the use of silicon carbide coatings on the graphite fuel sleeves to reduce the amount of graphite available for combustion. The other part of this study has been concerned with developing effective means of stopping the combustion should a situation ever arise when this would be necessary.

SUMMARY

With some small exceptions, the experimental program outlined above has been completed. The conditions under which the EGCR Burning Rig will ignite have been established and an analytical model has been developed which predicts these conditions. Because the Burning Rig cannot exactly duplicate the reactor situation the final prediction of the safety of the EGCR must rest on computer calculations employing the above analytical model.

No advantage in retarding combustion was found in using silicon carbide coated fuel sleeves. The negative results of these tests are due both to the particular geometry of the EGCR moderator and sleeves as well as to the fact that all sleeves tested contained imperfections in the coatings.

Chlorine has been demonstrated to be an effective agent for extinguishing graphite fires. Concentrations in air of about 1 percent have been observed to extinguish graphite fires at temperatures as high as 1000° C.

Details of the above testing program are given in five reports. (1-5)

OXIDATION OF LARGE BLOCKS OF GRAPHITE

Because laboratory experiments designed to measure the oxidation rate of graphite under various conditions, e.g., at different temperatures, in the

presence of gamma radiation, and at different oxygen pressures, are commonly conducted on relatively small pieces of graphite, it is necessary to consider how these data may be applied to the oxidation of large blocks of graphite. Graphite is a porous substance. As a result, the oxidation rate is not directly dependent on the geometric, or exterior, surface which is exposed to the oxygen, but rather upon the interior pore surface down to some effective depth below the exterior surface. This effective depth for oxidation depends upon diffusion of gas into the graphite and is a subject which has been treated in detail by previous investigators.⁽⁶⁾ If y is the oxidation rate of a very small piece of graphite (that is where the access of gas to the interior of the sample is not limited by diffusion), then the oxidation rate of a massive piece of graphite under the same set of conditions is given by the relationship⁽⁶⁾

$$\text{Rate (cm}^3 \text{ of graphite consumed/hr)} = 0.033A\left(\frac{^{\circ}\text{K}}{273}\right)^{0.38} \sqrt{y} \quad (1)$$

where A is the geometric surface area exposed to the coolant in square centimeters, and y must be expressed in fraction weight loss per hour. The constant term in Equation (1) depends to some extent on the type of graphite; experiments are now underway to improve the evaluation of this constant for EGCR graphite.

From observations on the oxidation rates of some 50 small samples of the EGCR moderator graphite, the following expression for y was developed.⁽¹⁾

$$y(\text{hr}^{-1}) = 6.91 \times 10^{-10} e^{-25,000/^{\circ}\text{K}} \quad (2)$$

Investigations of the oxidation rate of graphite proposed for use in the sleeves in the EGCR (Speer 901), have shown that the rates are nearly identical, that is within experimental error of $\pm 30\%$, with those of the EGCR moderator graphite. Thus, the above equation is also valid for the sleeve graphite. Equation (2) applies for air at one atmosphere pressure, and when used in Equation (1) closely predicts the oxidation rates observed in the Burning Rig. Near atmospheric pressure the oxidation rate was found to depend on the 0.7 power of the partial pressure of oxygen.

Another point which is important in the oxidation of graphite is the amount of prior oxidation that has occurred. Oxidation opens up the pores and increases the available surface for combustion. It has been found⁽¹⁾ that the rate of oxidation increases during the time that the first few percent of the carbon is being oxidized. After this initial period, the rate is not changed significantly until the graphite has been about 50 percent oxidized. This effect is illustrated in Figure 1. It can be expected that the graphite in the EGCR will be slowly oxidized over a period of years by impurities in the circulating helium. After a few percent oxidation, the higher oxidation rate should apply. Thus, in order to be conservative, the above rate equations are based on data obtained after the initial burnoff period and do not take into account the slower initial rate of oxidation.

FIGURE 1

Typical Graphite Weight Loss Curve Showing the Increase in Oxidation Rate During about the First 5 Per Cent Burnoff.

EGCR BURNING RIG EXPERIMENTS

Description of Burning Rig

Figure 2 is a cross section drawing of the Burning Rig configuration as the rig was assembled during some of the final combustion tests. A ring of EGCR moderator graphite containing four resistance heating elements is located at the outside. This outer ring simulates the moderator surrounding a single channel in the EGCR. The positioning of the four heating elements does not allow exact duplication of the temperature profile in the EGCR moderator; however, it does provide nonuniform heating patterns of the type that will occur in the reactor. In the actual reactor case, the point of maximum temperature would be moved radially outwards, thus giving a higher effective heat capacity than that obtainable in the Burning Rig. However, according to the calculations which have been made, this point of maximum temperature has no important effect on the ability of the Burning Rig to predict behavior of the EGCR.

The next feature of the Burning Rig, proceeding inwards, is the outer gas annulus where about 6.5 percent of the total coolant flow passes. In the last Burning Rig tests, it was possible to preheat this annulus air to a different temperature than the central air.

The graphite fuel element support sleeve comes next. In some tests the fuel element sleeves were coated with silicon carbide on the inner and outer surfaces. Prior to the time that sleeves were available, testing was done with a solid plug of graphite in the center containing heater rods. In a limited number of these preliminary tests the solid plug was covered with an iron pipe in order to afford only one surface, the moderator, for combustion. These early experiments are not described in detail in this summary report, but are outlined in Appendix II.

Inside of the fuel support sleeve is located a silicon carbide Global heating element. This Global element is capable of being heated to high temperatures and was used to simulate the radiant heat load from the fuel elements immediately after shutdown. The power input to this heating element was programmed to decrease with time in the same manner that the heat from the fuel elements would decrease with time.

Figure 3 shows a longitudinal section of the Burning Rig and indicates typical positioning of the thermocouples during a test. The large number of thermocouples was needed to determine which surfaces were burning as well as to follow any change in size or location of the burning area during the progress of the combustion test.

FIGURE 2

Transverse Cross Section of Burning Rig as Assembled During Tests 14 Through 18.

HW-71926

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FIGURE 3
Longitudinal Section of Burning Rig. Thermocouple Arrangement for Tests 13 Through 18.

Theoretical Considerations Involving Burning Rig Behavior

Before examining the results of the tests which were conducted in the Burning Rig, it is worthwhile to briefly consider what might be expected of this type of test. An analytical treatment, considerably more simplified than that used in transposing Burning Rig experience to predictions of reactor behavior, gives the following expression for the critical graphite temperature (T_c). If the graphite temperature is initially above T_c , the graphite will continue to heat upon the introduction of air, and if it is below T_c , it will cool.

$$\frac{C}{T_c} = \ln(\text{Rate}) - \ln(T_c - T_A) + \alpha \quad (3)$$

In the above equation, C is a constant which depends upon the activation energy for oxidation. Rate is that rate given by Equation (1). T_A is the local air temperature, α is a term which depends on the available surface area as well as the heat transfer coefficients, air flow and certain other factors. In connection with the above equation, it may be noted that the critical temperature is not linearly dependent upon the oxidation rate. Furthermore, as may be implied by direct reasoning or from Equation (3), the graphite will heat up if the coolant temperature is not less than that of the graphite. Under some conditions, this latter consideration is significant because the coolant may heat up to the graphite temperature near the outlet end of the coolant passage. In these cases, other heat losses, e.g., conduction of heat through the graphite, control the critical temperature, and it is very difficult to duplicate reactor conditions in the Burning Rig.

Since it is not possible to completely duplicate reactor conditions in the Burning Rig, it also follows that the conditions under which the Burning Rig ignites are not identical with conditions causing ignition in the reactor. As an example, in early Burning Rig experiments without central cooling, i.e., a solid core replacing the fuel sleeve, self-sustained combustion was observed at graphite temperatures as low as 410° C. In this case control of radial heat losses was very important. However, the differences between the rig and the EGCR have been taken into account by the analytical treatment, and it is believed that the extrapolation to reactor conditions can be made on a sound basis. Basically the extrapolation is performed with Equation (3), but taking into consideration the initial non-isothermal situation in the reactor and the transient conditions which would follow a coolant line rupture.

Initial Burning Rig Tests

The first Burning Rig tests⁽²⁾ demonstrated that trends in behavior observed in laboratory testing also applied to situations where large blocks of graphite were being oxidized. As an example, in the laboratory testing, prior oxidation was shown to have a large effect on oxidation rate. In Figures 4 and 5 are illustrated temperature rises observed in the Burning Rig with a solid graphite core. In the experiments illustrated, the initial temperature distributions were approximately the same, but in one test (Figure 4) there was essentially no prior oxidation and in the other (Figure 5) there was a considerable amount of prior oxidation. It can be seen that the pre-oxidized column showed quite rapid heating whereas the unoxidized column heated more slowly.

FIGURE 4

Temperature Rises in the Burning Rig During Experiment 10-3. In This Test There was Very Little Previous Oxidation of the Graphite

FIGURE 5

Temperature Rises in the Burning Rig During Experiment 10-11. In This Test There Was Considerable Preoxidation of the Graphite

HW-71926

Another important observation was that the depth of oxidation was close to that predicted by the analytical model. In Figure 6 is shown a cross sectioned piece of graphite from the solid core in the rig. The oxidized outer surface is easily discerned and indicates the general validity of the analytical treatment in considering that the reaction occurs only to a specified depth below the graphite surface.

Additionally, it was demonstrated that it was not possible, even at maximum EGCR coolant flows, to blow out the fire in the Burning Rig once such a fire has been started. In Figure 7 the graphite temperature at the mid-plane of the column as a function of time is shown. After combustion was initiated, the air flow was increased some 15 fold. Instead of the fire going out, it was greatly enhanced and a very rapid increase in temperature was observed. This occurred even after all electrical power to the rig has been cut off allowing considerable radial heat loss. At 120 minutes, the air flow was completely stopped allowing the fire to smother itself. However, upon reinstatement of the air flow at a later time, the fire rapidly rekindled. Once a fire has started, the increased oxygen supply provided by the higher air flow more than compensates for the increase in the amount of cooling that can be provided by the extra air. This effect should be expected when there is an abundant supply of oxygen since the oxidation rate will increase exponentially with temperature, whereas the heat removal efficiency increases only approximately linearly with the graphite temperature.

Maximum Credible Accident Experiments

The final tests⁽³⁾ were conducted to simulate as closely as possible the maximum credible accident conditions in the EGCR. In these tests, fuel sleeves were used as well as the central Globar heating element. Reactor air flow, inlet air temperature, moderator temperature, and after-heat decay for the following accidents were duplicated.

Experiment 15-1	Moderator temperature	625° C
	Outer surface fuel sleeve temperature	670° C
	Inlet air temperature (center)	350° C
	Total air flow	372 lb/hr
Experiment 15-2	Moderator temperature	590° C
	Outer surface fuel sleeve temperature	625° C
	Inlet air temperature (center)	450° C
	Total air flow	186 lb/hr
Experiment 15-3	Moderator temperature	690° C
	Outer surface fuel sleeve temperature	720° C
	Inlet air temperature (center)	425° C
	Total air flow	287 lb/hr

The channel cooled under every set of test conditions.

FIGURE 6

Cross Sectioned Graphite from Burning Rig. Mag. = 5X

FIGURE 7

Effect on Burning Rate of Increasing Air Flow After Combustion has been Initiated.

Further tests were run to determine conditions under which self-sustained combustion could be initiated. At a flow of 287 lb/hr, combustion occurred in the assembly when the moderator temperatures were greater than 710 C.

The above experiments are merely an illustrative sampling of the large number of tests which were conducted with bare graphite fuel sleeves or solid central sleeves. The conditions in the tests are summarized in Appendix II, and a detailed report of the experimentation is given in References 2 and 3.

LABORATORY SCALE EXPERIMENTS

Effects of Gamma Radiation

It is known that under certain conditions, gamma radiation can enhance the oxidation rate of graphite with various gases. In order to investigate the importance of this effect, a series of tests were conducted⁽¹⁾ in the presence of a 1×10^6 r/hr gamma flux and in the temperature range of 450° to 650° C. Experiments to date have been conducted on CSF graphite (a type of purified reactor grade graphite) rather than on EGCR graphite. Figure 8 illustrates the increase in oxidation rate observed in the presence of gamma radiation. The results in Figure 8 were obtained in air at one atmosphere of pressure; similar results were obtained in pure oxygen. It is noted that the radiation enhanced reaction has a smaller dependence on temperature than the purely thermal reaction. Thus, above about 650° C, the presence of gamma radiation is of little practical significance. From the data in Figure 8, and from relationships between the oxidation rate of CSF and EGCR graphite, the following expression was derived for the reaction rate of EGCR graphite in the presence of ionizing radiation.

$$y = 8.3 \times 10^5 e^{-14,700/^{\circ}K} \quad (4)$$

Experiments are in progress to determine the effect of gamma flux intensity on the oxidation rate. The preliminary data indicate that the dependence on flux intensity is less than first order and additional experiments are in progress to establish the exact relationship.

Effect of Prior Irradiation of Graphite

Neutron bombardment of graphite prior to oxidation has been reported⁽⁷⁾ to increase the oxidation rate of the graphite. This effect, however, is annealable and should therefore depend upon the irradiation temperature. No data have previously been reported on samples irradiated above room temperature. Therefore, a series of samples were oxidized⁽¹⁾ that had been irradiated to an exposure of 10^{20} nvt ($E > 0.1$ Mev), at temperatures of 550° C or higher. When oxidized, these samples showed no discernible difference in rate from those of unirradiated samples.

Tests are underway to oxidize samples which have been exposed to 20 to 30 times the dose of the above samples. No results from these tests are yet available.

FIGURE 8

Oxidation Rate of CSF Graphite Without Radiation Present and in the Presence of 10^6 r/hr Gamma Radiation. Tests in Air at 1 Atmosphere Pressure

Effect of Impurities on Oxidation Rate

Metallic impurities, particularly iron and vanadium, are known to have a considerable influence on the rate of oxidation of graphite.⁽¹⁾ From the standpoint of oxidation, EGCR graphite is not particularly pure and oxidized EGCR graphite shows a pitted appearance which is characteristic of impurity catalysis. Figure 9 demonstrates the appearance of EGCR graphite oxidized in air at 600° C for 24 hours as compared with a piece of high purity graphite oxidized at the same time. The importance of conducting the oxidation tests with actual EGCR graphite, or at least a graphite equivalent in reactivity, is thus indicated. In all cases where testing was conducted with non-EGCR graphite, a correction was applied to normalize the oxidation rates to those which should be observed with EGCR graphite. The derivation of Equation (4) is an example of such a correction.

It is also possible that impurities deposited on the graphite, such as fission products or iron carried from other parts of the system, may catalyze the oxidation. No studies have been conducted on oxidation of graphite doped with fission products. However, the presence of additional impurities on the already relatively impure EGCR graphite would not be expected to have as much influence upon oxidation as in the case where these impurities were deposited on an initially very pure graphite.

Effects of Water Vapor on the Combustion Rate

Moisture has a slight catalytic effect on the oxygen-graphite reaction. Because it is possible that a steam coil rupture may occur at the same time that air is introduced into the reactor, experiments were conducted in the laboratory in which 14.5 weight percent of water was added to the air during the oxidation experiments. This is the amount of water calculated to result from a steam coil leak. Between about 550° and 700° C, this much water was found to increase the reaction rate approximately 40 percent, but this order of increase is just on the fringe of normal experimental error, and is not considered to be too significant.

Tests were also run in the Burning Rig⁽²⁾ in which the moisture content of the air was varied between very dry, i.e., less than 0.05 weight percent, to humid, i.e., approximately 1.5 weight percent moisture in the air. There was no discernible difference in the combustion behavior with the dry and the humid air.

A

B

FIGURE 9

Comparison of Appearance of (A) EGCR and (B) Gas Purified Graphite After Oxidation in Air
at 600⁰ C for 24 Hours. Mag. = 4X

EXTRAPOLATION OF BURNING RIG AND LABORATORY TESTS TO THE EGCR CONDITIONS

Based on the above equations for oxidation rates, computer codes have been developed by Allis-Chalmers and ORNL which predict the combustion characteristics of the EGCR. These codes must, of course, take into account the heat distribution, heat transfer coefficients, and transient flow and heat generation conditions in the EGCR. Because the Burning Rig experiments duplicated the conditions in the EGCR as closely as was practical, a good test of the computer code was to check its ability to predict ignition temperatures and rates of temperature rise in the Burning Rig. A comparison of computer predictions to Burning Rig behavior was made in the Allis-Chalmers Study IV-324.⁽⁸⁾ Good agreement between the experimental and analytical approaches was indicated.

At this time, however, there are certain factors which must be taken into account in the computer calculations and which cannot be completely evaluated from the experiments. Thus, if a conservative calculation of combustion conditions is to be performed, the following factors should be considered in computing the oxidation rate. The first concerns the effect of gamma flux intensity. At temperatures above 650° C, experiments indicate that the burning rate is increased less than a factor of two by the presence of 10^6 r/hr gamma radiation. The effect of gamma radiation at different intensities is not well defined. Since the gamma flux in reactor immediately after shutdown is probably higher than 10^6 r/hr, a correction factor for gamma radiation of a factor of three at 650° C should be applied to give a conservative calculation. This is believed to be an adequate correction factor, particularly since the importance of radiation rapidly decreases above 650° C. The second point to consider is the effect of deposited impurities such as fission products on the graphite. This is a difficult consideration to correct for accurately, but such impurities would not be expected to increase the rate any more than a factor of three. The next point is the effect of water vapor due to a steam coil leak. The increase in rate of 40 percent as evidenced in laboratory experiments is believed to be adequate to cover this contingency. One last point should be mentioned; very long neutron exposures may increase the reactivity of the graphite. However, this is not regarded as likely and no correction factor for the effect is recommended. Therefore, if all the above factors are considered to be independent of temperature, the total correction to be applied to the laboratory oxidation rates is a factor of $3 \times 3 \times 1.4$ or 13. The computer calculations can treat the situation in more detail and take into account the fact that the contribution of gamma radiation decreases as the temperature increases. Experiments are now underway to narrow the uncertainty in the above factors as much as possible.

INVESTIGATIONS OF THE USE OF SILICON CARBIDE COATED FUEL SLEEVES TO RETARD OXIDATION

Silicon carbide is highly resistant towards oxidation and can be bonded to several types of graphite. To provide maximum protection to the graphite

substrate, the silicon carbide is normally impregnated with silicon to reduce the porosity of the coating. Such a coating is called siliconized-silicon carbide.

There are three important requisites for the use of siliconized-silicon carbide coatings on graphite: (1) the graphite must have the proper porosity so the coating will bond to it, (2) the coefficients of thermal expansion of both the coating and the graphite must be similar so that the coating will not crack or spall during thermal cycling (for practical purposes, this requires that a rather isotropic grade of graphite be used), (3) the graphite must be relatively stable towards radiation-induced dimensional changes so that it will not shrink and cause the coating to crack. The last two requirements, i.e., isotropy and radiation stability, greatly narrow the range of graphites that can be used, but at least one commercially available, satisfactory grade of graphite has been found, Speer 901.

The majority of the Hanford work on investigating coated graphites⁽⁵⁾ is only indirectly related to the EGCR problem, and these studies are summarized in Appendix I. The most pertinent point of these studies is the demonstration that siliconized-silicon carbide coated graphite could most likely be used in the EGCR without any degradation of the coating quality. There is still a problem, however, of obtaining coated sleeves of initially perfect quality on a production basis.

As far as the Hanford work is concerned, the direct evaluation of coatings on EGCR fuel sleeves has been done exclusively in the Burning Rig. Preliminary experiments were directed towards determining how much the combustion would be retarded if only one combustion surface, the moderator, were exposed to the air. These tests were accomplished by replacing the solid graphite plug in the center of the column with a steel clad graphite plug; thus for these tests there was no central coolant flow. A reduction in the tendency for the Burning Rig to ignite was noted; results are summarized in Appendix II. All of the Burning Rig tests which utilized a solid plug in the center of the rig rather than a fuel sleeve were severe tests inasmuch as a very important heat path was not present. That path is for the transfer of heat from the burning annulus region, through the fuel sleeve by conduction, and into the coolant in the central channel. This additional cooling is particularly important since about 94 percent of the coolant passes through the central channel.

The comparison of combustion characteristics of the reactor with coated and uncoated fuel sleeves should be made based on the Burning Rig experiments in which actual fuel sleeves were used. One of the first such tests in the Burning Rig was to duplicate several maximum credible accident conditions using silicon carbide coated sleeves. These sleeves did not have perfectly continuous coatings, but they were the best available. Some of the behavior observed below was probably modified by oxidation of the sleeves through the

flaws in the coating. Reactor after-heat decay functions were programmed as power input to the radiant heating element in the center of the fuel channel. The tests and observations were as follows:

Experiment 14-1 Initial Conditions:

Moderator temperature	615° C
Outer surface fuel sleeve temperature	630° C
Inlet air temperature (center)	225° C
Total air flow	372 lbs/hr

Observations: Assembly cooled; slowest rate
observed was 2° C/min

Experiment 14-2 Initial Conditions:

Moderator temperature	615° C
Outer surface fuel sleeve temperature	630° C
Inlet air temperature (center)	425° C
Total air flow	186 lbs/hr

Observations: Assembly cooled; slowest rate
observed was 0.5° C/min

Experiment 14-3 Initial Conditions:

Moderator temperature	685° C
Outer surface fuel sleeve temperature	700° C
Inlet air temperature (center)	400° C
Total air flow	287 lbs/hr

Observations: Moderator temperatures at mid-plane and above rose for the first five minutes to about 720° C, remained constant for about 20 minutes and then began to fall. The SiC coated fuel sleeves apparently did not fail since cooling of the sleeves was noted almost immediately after air was introduced.

Although each of these tests indicated a safe condition, i.e., the graphite cooled, there was no apparent advantage to the behavior of the coated sleeves over the uncoated sleeves; compare the above results with those on page 11.

Other tests were conducted⁽³⁾, see Appendix II, to examine the combustion characteristics of the Burning Rig with silicon carbide coated sleeves. Again, these tests did not show any obvious advantage of using the coating. Consequently a final set of tests were run to check the relative merits of coated and uncoated fuel sleeves. In these tests, there were two series of runs; the

first with silicon carbide coated sleeves and the second with uncoated fuel sleeves. Initial conditions were repeated as closely as possible for corresponding tests in each series. Data are tabulated below.

<u>Experiment</u>	<u>Initial Condition</u>		<u>Observed Rate of Temperature Rise (°C/min)</u>
	<u>Maximum Graphite Temp (°C)</u>	<u>Total Air Flow (lb/hr)</u>	
16-1)	605	378	- 0.5
16-2)	624	186	- 0.05
16-3) Coated sleeves	684	287	+ 2
16-4)	624	100	+ 1
16-5)	678	186	+ 2
17-1)	632	378	- 1.7
17-2)	615	186	- 1
17-3) Uncoated sleeves	691	287	- 1
17-4)	616	100	+ 0.2
17-5)	670	186	+ 0.5

Figures 10 and 11 show the transient behavior of various temperatures that were recorded during Experiments 16-3 and 17-3 above. The similarity of behavior in the two cases is noted. On the basis of all the above data, there is no apparent advantage to using coated sleeves, since the Burning Rig showed no increase in stability towards combustion with coated sleeves.

In Figure 12 is a photograph of one of the silicon carbide sleeves that was used in Experiment 12 and which was rather severely damaged during combustion. The undermining of the coating originated at a defect that was present in the sleeve before testing was initiated. This indicates that any advantage which could be gained by using silicon carbide coated sleeves may be lost if the original sleeves contain small defects because the defected area will rapidly enlarge due to local burning. Imperfections in the sleeves and behavior such as illustrated probably contributed to the ineffectiveness of the sleeves in the Burning Rig tests.

FIGURE 10
 Temperature Rises in Burning Rig During Experiment 16-3. In this Experiment the Fuel Sleeves were Coated with Silicon Carbide

HW-71926

FIGURE 11
 Temperature Rises in Burning Rig During Experiment 17-3. In this Experiment the Fuel Sleeves were Uncoated

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FIGURE 12

Badly Damaged Silicon Carbide Coated Fuel Sleeve After Combustion Tests. The Undermining of the Coating is believed to have Initiated at a Flaw in the Coating Initially Located at the End of the Sleeve

EFFECT OF CHLORINE IN EXTINGUISHING GRAPHITE-OXYGEN FIRES

Extensive laboratory testing has been conducted,⁽⁴⁾ on the effect of chlorine in extinguishing graphite fires. It has been found that the oxidation rate in the presence of chlorine follows the rate law in Equation (5).

$$y = \frac{k_1}{(Cl_2/O_2)^{1/2} + k_2} \quad (5)$$

where k_1 and k_2 are constants. In accordance with this law, the addition of the first few percent chlorine is found to drastically reduce the oxidation rate; one volume percent chlorine in oxygen cutting the rate about in half.

The effectiveness of chlorine was demonstrated on a small scale by igniting in an oxygen stream cylinders of graphite about 1 inch in diameter and then, when the fire became very rapid, introducing small amounts of chlorine. Results of such an experiment are shown in Figure 13. The rapid temperature rise after the graphite ignited is in evidence. After about 20 minutes the thermal insulation surrounding the sample chamber was removed so that the burning graphite could be viewed; this action permitted some radial loss of heat so that the rate of temperature rise decreased. At about 25 minutes, approximately one percent chlorine was added, the visible flames immediately extinguished and the graphite started to cool.

It was considered important to determine whether the chlorine would also be an effective inhibitor in the presence of ionizing radiation. The primary effect of radiation is to produce active species in the oxygen, and it was not known whether these would be too reactive with graphite for the chlorine to have any significant effect in retarding the oxidation. Consequently, tests were run in which the graphite was oxidized in ozone; ozone is similar in reactivity to the species formed under irradiation. Chlorine was found to be as effective an inhibitor as in the previous tests where the chlorine was added to oxygen. In another series of tests the graphite was oxidized in the presence of a 10^6 r/hr gamma field during the time that the chlorine was introduced. Again, the chlorine was found to have the same effectiveness in reducing the oxidation rate.

Based on the above results, it is reasonable to assume that an in-reactor fire could be extinguished by the addition of small amounts of chlorine. As an additional experiment for the EGCR case, tests are planned in which chlorine will be introduced to the Burning Rig after it is caused to ignite.

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Nonmetallic Materials Development Operation
Hanford Laboratories Operation

FIGURE 13

Effect of Chlorine Addition on the Combustion of a Small Piece of Graphite

APPENDIX I

SUMMARY OF WORK ON SILICONIZED-SILICON CARBIDE COATINGS

Continuous siliconized-silicon carbide coatings on graphite are effective protection against oxidation at temperatures over 1000° C. If the coating is applied on an isotropic base graphite, the coefficients of thermal expansion match closely enough so that there is no degradation of the coating due to thermal cycling. The stability of the coating has been demonstrated⁽⁵⁾ by thermal cycling samples between 250° and 1200° C in flowing air. Approximately 30 samples of different geometries; rod, balls, and prisims have been cycled along with other coated samples which had been previously irradiated. These latter samples were irradiated to an exposure of approximately 3000 MWD/AT at about 500° C. Data from these thermal cycling tests are given below.

THERMAL CYCLE TESTING - Si-SiC COATING ON GRAPHITE
250° C - 1200° C - FLOWING AIR

Unirradiated Coated Graphite

<u>Cycle Frequency</u>	<u>Hours</u>	<u>% Wt. Change</u>	<u>+ Hours</u>	<u>% Wt. Change</u>	<u>+ Hours</u>	<u>% Wt. Change</u>
6 cys/hr	33	+0.656	69	+0.043	97	+0.030
6 cys/hr	75	+0.005	119	+0.004	115	0
5 cys/hr	28	+0.028	65	+0.013	48	+0.011
6 cys/hr	58	+0.007				
7 cys/hr	69	+0.010	146	+0.018	150	+0.008

Irradiated Coated Graphite

<u>Cycle Time</u>	<u>Number of Cycles</u>	<u>% Weight Change</u>
117 hrs	824	+0.003)
96 hrs	670	-0.002)
103 hrs	779	+0.0003)

) Variable
cycle
frequency

The above data were all taken on samples which are regarded as having good initial coatings on the proper types of base graphite. It is noted that under the rather severe test conditions, there were no failures of the coatings.

In addition to the thermal cycle testing, experiments were conducted in which coatings laid down on various types of graphites were irradiated. It was found that of the isotropic graphites tested Speer 901 was the only graphite, commercially available at the present time, which did not contract to a degree where the integrity of the coating was lost due to cracking. Because Speer 901 graphite has not been as well characterized under radiation as normal moderator grade graphites or the EGCR moderator graphites, irradiation testing of this graphite was conducted in the ETR. Samples were irradiated between 1200° and 1400° C to EGCR equivalent exposures of about 5000 MWD/AT. The results showed that the Speer 901 contracted slightly more in the direction parallel to the extrusion axis than in the transverse direction but showed considerable isotropy with the ratio of transverse to parallel contraction being only 0.6. By way of comparison, EGCR moderator graphite irradiated simultaneously showed approximately the same contraction rate as the Speer 901 in the parallel direction. It is interesting to note that both the Speer 901 and the (National Carbon Co.) EGCR moderator graphite are relatively stable towards radiation-induced contraction.

In one additional test of the coatings, coated graphite samples are being prepared for irradiation to very high exposures in the ETR. This test will determine if there is any unexpected degradation of the coating after long exposures.

APPENDIX II

SUMMARY OF BURNING RIG TESTS AND OBSERVATIONS

<u>Experiment</u>	<u>Total Air Flow, lb/hr*</u>	<u>Inlet Air Temp, °C</u>		<u>Initial Max. Graphite Temp, °C</u>		<u>Heating Rate, °C/min</u>
		<u>Annulus</u>	<u>Center</u>	<u>Moderator</u>	<u>Sleeve or Core</u>	
1 - Solid central core; Speer Nuclear Grade II graphite; predried air; heaters off during runs						
1-1	4	20	--	635	635	- 0.50
1-2	55	220	--	650	650	- 0.50
1-3	55	220	--	715	715	+ 5.4
1-4	55	20	--	735	735	+ 7.3
2, 3, and 4 - Same, except heaters controlled to give adiabatic conditions during experiments						
2-1	4.4	20	--	410	410	+ 0.08
2-2	4.4	20	--	440	440	+ 0.33
2-3	4.4	20	--	470	470	+ 0.25
2-4	19.0	20	--	460	460	+ 0.17
2-5	19.0	20	--	640	640	+ 1.3
2-6	54.5	20	--	680	680	+ 3.3
3-1	4 to 60	220	--	610	610	rise
4-1	4 to 60	220	--	425	425	rise
4-2	55	220	--	700	700	+ 9.8
5 - New graphite assembly; solid central core; Speer Nuclear Grade II; predried air; heaters off during runs						
5-1	4	180	--	475	475	- 0.16
5-2	4	170	--	530	530	- 0.16
5-3	4	180	--	570	570	- 0.16
5-4	4	185	--	600	600	- 0.16
5-5	4	200	--	630	630	- 0.08
6, 7, and 8 - Same, except heaters controlled to give adiabatic conditions during runs						
6-1	4	130	--	480	480	+ 0.25
6-2	4	140	--	535	535	+ 0.25

SUMMARY OF BURNING RIG TESTS AND OBSERVATIONS--Continued

Experiment	Total Air Flow, lb/hr*	Inlet Air Temp, °C		Initial Max. Graphite Temp, °C		Heating Rate, °C/min
		Annulus	Center	Moderator	Sleeve or Core	
7-1	4	120	--	450	450	+ 0.33
7-2	20	110	--	460	460	+ 0.08
7-3	20	145	--	590	590	+ 0.27
7-4	20	150	--	640	640	+ 1.5
7-5	55	110	--	695	695	+ 4.7
8-1	4	120	--	410	410	0.00
8-2	4	120	--	445	445	+ 0.16

9 - Same, except heaters off during run

9-1	4	120	--	600	600	- 1.7
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10 - New graphite assembly; National Carbon Co. graphite; predried air except after Experiment 10-13; heaters controlled to give adiabatic conditions during runs

10-1	4	20	--	450	450	+ 0.16
10-2	4	20	--	585	585	+ 0.16
10-3	4	20	--	550	550	+ 0.16
10-4	4	20	--	575	575	+ 0.13
10-5	4	120	--	525	525	+ 0.08
10-6	20	20	--	530	530	+ 0.03
10-7	20	120	--	555	555	+ 0.42
10-7A	20	120	--	630	630	+ 1.1
10-8	4	20	--	700	700	+ 0.42
10-9	4	20	--	700	700	+ 0.50
10-10	12	20	--	580	580	+ 1.5
10-11	15	20	--	550	550	+ 1.4
10-12	4	20	--	625	625	+ 0.42
10-13	4	20	--	550	550	+ 1.0
10-13A	4	20	--	625	625	+ 0.92

Air predrier removed

10-14	4	20	--	540	540	+ 1.3
10-15	4	20	--	615	615	+ 0.8
10-16	15	20	--	670	680	+ 5.0
10-17	15	20	--	585	585	+ 1.3
10-17A	4	20	--	665	670	+ 0.67
10-18	35	20	--	600	600	+ 2.0

SUMMARY OF BURNING RIG TESTS AND OBSERVATIONS--Continued

Experiment	Total Air Flow, lb/hr*	Inlet Air Temp, °C		Initial Max. Graphite Temp, °C		Heating Rate, °C/min
		Annulus	Center	Moderator	Sleeve or Core	
11 - New graphite assembly; solid core enclosed in stainless steel tube; National Carbon Co. graphite; heaters controlled to give adiabatic conditions during runs						
11-1	4	20	--	600	600	- 0.58
11-2	4	20	--	520	520	+ 0.20
11-3	4	20	--	565	565	+ 0.08
11-4	4	20	--	650	650	+ 0.33
11-5	4	20	--	700	700	+ 0.42
11-6	4	20	--	500	505	+ 0.25
11-7	4	20	--	560	565	+ 0.67
12 - New graphite assembly; silicon carbide coated fuel sleeves containing dummy fuel elements (no central heating element); actual EGCR moderator graphite; guard heaters maintained at constant power during test (initially adiabatic conditions) except 12-4; run with power off						
12-1	186	20	20	500	500	- 0.67
12-2	186	20	20	645	655	- 1.7
12-3	186	20	20	720	720	+ 7.0
12-4	186	20	20	680	680	- 3.3
12-5	186	20	20	625	625	- 2.5
12-6	186	20	20	650	655	0
12-7	93	20	20	540	540	- 0.6
12-8	93	20	20	660	670	+ 1.7
12-9	186	20	20	950	950	+ 1.7
13 - New assembly; reused EGCR moderator and coated sleeves; dummy fuel elements removed; remainder of conditions same as above						
13-1	186	20	20	665	670	+ 0.16
13-2	186	20	20	685	690	- 0.50
13-2	186	20	20	730	730	+ 1.7
14 - New silicon carbide coated sleeves and EGCR graphite; central heating element installed and operated with programmed power decay; guard heaters maintained at constant power						
14-1	372	20	385	615	630	- 1.8
14-2	186	20	425	605	615	- 0.50
14-3	287	20	400	684	697	rise then drop
14-4	287	20	430	747	757	+ 6.5
14-5	287	20	400	694	706	+ 1.7

SUMMARY OF BURNING RIG TESTS AND OBSERVATIONS--Continued

Experiment	Total Air Flow, lb/hr*	Inlet Air Temp, °C		Initial Max. Graphite Temp, °C		Heating Rate, °C/min
		Annulus	Center	Moderator	Sleeve or Core	
15 - New assembly; experiments same as above, except that uncoated sleeves are used						
15-1	372	20	350	626	672	- 1.0
15-2	186	20	450	592	605	- 0.20
15-3	287	20	425	688	720	- 0.20
15-4	287	20	415	710	736	+ 2.8
16 - New assembly; experiments same as above, except that silicon carbide coated sleeves containing slots and holes to center fuel elements were used						
16-1	378	150	260	605	610	- 0.50
16-2	186	60	400	624	629	- 0.05
16-3	287	100	320	684	690	+ 2.0
16-4	100	80	400	624	630	+ 1.0
16-5	186	100	320	672	678	+ 2.0
17 and 18 - New assembly; experiments same as above, except that uncoated sleeves were used						
17-1	378	100	410	632	636	- 1.7
17-2	186	100	300	615	619	- 1.0
17-3	287	100	300	691	697	- 1.0
17-4	100	80	400	616	620	+ 0.2
17-5	186	100	400	670	676	+ 0.5
18-1	378	115	265	621	625	- 1.0
18-2	186	150	400	613	619	+ 0.13
18-3	287	140	300	730	735	+ 5.0

* In each experiment where the flow was split between the annulus and central flow channel, 6.5 percent of the flow was directed up the annulus.

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