GRAPHITE FOR HELIUM-COOLED REACTORS
A REVIEW

G.L. Tingey and W.C. Morgan

Battelle

Pacific Northwest Laboratories
Richland, Washington 99352

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G. L. Tingey and W. C. Morgan

Ceramics and Graphite Section
Fuels and Materials Department

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ABSTRACT

This review encompasses information on the manufacture of nuclear graphites, including the improved isotropic grades, the physical, chemical, and morphological differences among these materials, the theory of radiation-induced changes as influenced by morphology, and available data on radiation-induced changes in dimensions, physical properties, and chemical reactivity. The review also includes information on neutron dosimetry, carbon displacement cross sections, and the general problem of transposing data from one reactor to another. In lesser detail, information on other materials, such as boron carbide, non-graphitized carbons, and pyrolytic carbon coatings, is reviewed with respect to possible use and performance in a HTGR.

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LIST OF SYMBOLS

(This list contains only those symbols used repeatedly in the text)

$\frac{dc}{dt}$ = Time rate of carbon gasification.

R = Gas constant.

T = Temperature in degrees Kelvin.

P_i = Partial pressure of gas i.

k_j = Rate constant j in rate expression.

D_{eff} = Effective diffusion coefficient.

$d\chi_c$ = Length change per unit length and unit fluence for crystallites in the direction transverse to the basal plane.

$d\chi_a$ = Length change per unit length and unit fluence for crystallites in the direction parallel to the basal plane.

LIST OF ABBREVIATIONS

DRAGON = OECD Helium Cooled Test Reactor - Winfreth, England.
 HFIR = High Flux Isotopes Reactor.
 DIDO = Heavy Water Moderated Test Reactor - Harwell, England.
 EURATOM = European Atomic Energy Community
 OECD = European Nuclear Energy Agency (ENEA)
 THTR = Thorium High Temperature Reactor

GRAPHITE FOR HELIUM-COOLED REACTORS--A REVIEW

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I. INTRODUCTION

The potential advantages of high temperature gas-cooled reactors (HTGR's) and the rationale which resulted in current power reactor designs has been adequately documented by others,⁽¹⁻¹⁰⁾ and will not be covered here. The common characteristics of the several specific reactor designs are: 1) The use of helium as the coolant; 2) The application of graphite as the primary structural material; and 3) The use of carbon coated ceramic fuel particles. In addition to the primary use of graphite for structural support and neutron moderation, it is used along with other carbon materials as the neutron reflector and shield, the core support blocks, the coatings on fuel particles, and the matrix material for the fuel beads and control rods. Thus, the performance of the graphite and carbon is of utmost importance to the satisfactory operation of the reactor.

Although this document is primarily directed at a review of information on core-grade nuclear graphite, data on other materials such as boron-carbide, non-graphitized carbons, and pyrolytic carbon coatings are reviewed with respect to possible uses and performance of these materials in an HTGR.

Delle⁽¹¹⁾ has made an extensive review of the theories of radiation-induced dimensional changes of all types of graphites and reported the results of an experimental program to test these theories. Other recent reviews have been made by Kasten et al.,⁽¹²⁾ Engle and Eatherly,⁽¹³⁾ Baker,⁽¹⁴⁾ and by Bokros et al.⁽¹⁵⁾ Extensive compendia of irradiation data have been published by Helm,⁽¹⁶⁾ Morgan and Grey,⁽¹⁷⁾ Everett et al.,^(18,19) and by Blackstone et al.⁽²⁰⁾ Earlier reviews and/or compilations of data which still have considerable application to HTGR's include Nightingale,⁽²¹⁾ Simmons,⁽²²⁾ Reynolds,⁽²³⁾ Bell et al.,⁽²⁴⁾ and two papers by Kelly et al.^(25,26)

In addition to the radiation behavior of carbon and graphite in the HTGR environment, the chemical behavior is of major concern. In contrast to its excellent high temperature physical properties, graphite is highly reactive to many chemicals at HTGR temperatures. Thus, to prevent reactions, very pure helium is used as the reactor coolant. Economic as well as technical considerations require that reasonably accurate predictions of the reactivity of the materials be made during the design phase of a HTGR plant. To enable these predictions to be made, data must be gathered from a variety of sources in the literature. Some excellent sources for basic kinetic data on the reactivity of carbons and graphite include reviews by Walker and Co-workers⁽²⁷⁾ and by Clark et al.⁽²⁸⁾ In addition, the Euratom group at DRAGON has reviewed the carbon transport problem as it specifically applies to HTGR's.⁽²⁹⁾

After five years operation of the Peach Bottom HTGR, a clearer understanding of the coolant composition and of impurity sources for a power producing helium-cooled reactor exists. These data have recently been published by Burnette⁽³⁰⁾ and his associates at Gulf General Atomics.

Although it is not within the scope of this report to describe in detail the requirements for the purification plant, this plant should be recognized as the major means for controlling the accumulation of carbon monoxide and hydrogen, as well as long-lived fission gases, in the helium coolant. A summary description of the purification plant for the Peach Bottom and the Fort Saint Vrain HTGR's has been given by Gittermann.⁽³¹⁾

In this report we have attempted to review the literature, drawing upon the most significant data pertaining to the graphite and carbon performance in the HTGR environment. We have not intended to supply a comprehensive review of the literature but rather to supply the reader with enough information to enable him to evaluate the performance of graphite in meeting reactor requirements safely and continuously.

II. PETROLEUM COKE BASED NUCLEAR GRAPHITES

MANUFACTURING

The manufacturing technology for nuclear-grade graphites developed from manufacturing processes used to produce high-purity electrode graphites.⁽³²⁻³⁴⁾ The primary differences are that higher purity is attained by judicious selection of raw materials, with greater emphasis being placed on safeguards to ensure against contamination and with augmented quality control procedures being used at all steps of the manufacturing process. In this section, we will consider only normal nuclear grade graphites (i.e., those which are based on calcined petroleum cokes produced by modified electrographite manufacturing technology); graphites based on uncalcined (raw) petroleum cokes, gilsonite cokes, and asphalt-based cokes will be discussed in the section on "Improved Nuclear Graphites". Typical processing procedures in the manufacture of a nuclear-grade graphite might involve the following steps:

- Petroleum coke, produced and calcined at the refinery, is crushed and screened to obtain a series of graded sizes of calcined particles; the finest particles are charged into a mill, where they are further reduced to a "flour".
- Coke particles, flour, coal tar pitch, additives (if used), and lubricating oil are mixed at 165-170°C and then extruded in the desired shape. A normal mix might consist of 50 to 60% flour, 15 to 20% particles, 20 to 25% pitch and 2 to 3% lubricating oil.
- The extruded "green" bodies are placed in a gas-fired furnace and, over a period of about three weeks, the temperature is slowly raised to between 750 and 1000°C; during this time the binder pitch pyrolyzes and the body shrinks by about 5%.

- After cooling, the baked bars are transferred to a vacuum-pressure autoclave for pitch impregnation; the autoclave is heated and evacuated to remove air from the pores in the carbon body. The autoclave is next filled with molten pitch and pressurized for several hours to ensure penetration of the pitch.
- Unless multiple impregnations are desired, the impregnated carbon bars are normally loaded directly into the graphitization furnace. The Acheson graphitization furnace consists of a horizontal bed of fire brick with electrodes at each end of the bed; the baked bars are stacked transversely between the electrodes with the spaces between stacks of bars being filled with granulated coke. The pack of bars, surrounded by finely ground silicon carbide, coke and sand to provide thermal insulation, is electrically heated to a peak temperature between 2400 and 3000°C.
- Most impurities are vaporized and removed at graphitization temperatures; however, the concentrations of other important impurities such as boron and vanadium are not substantially reduced by this treatment. Impurity levels of these materials must either be controlled by very careful selection of raw materials or through chemical purification. The purest nuclear graphites are produced by reacting halogens with impurities during graphitization. However, careful selection of raw materials and control of handling techniques are still required to assure the highest nuclear purity of the finished graphite.

The kinetics and mechanism of graphitization have been recently reviewed by Fischbach⁽³⁵⁾ and Pacault⁽³⁶⁾ and the effects of catalysts and other additives on the graphitization process have been described by Marsh

and Warburton⁽³⁷⁾ and Richards and Kellett.⁽³⁸⁾ Therefore, we shall confine our remarks to a brief discussion of the principle ingredients (petroleum coke, coal tar pitch, impregnating pitch, lubricating oil, and additives) of electrographites and normal nuclear grade graphites, and their role in determining the properties and behavior of the finished graphite body.

Petroleum coke, the primary ingredient used in the manufacture of electrographites, is a by-product of petroleum refining. Practically all petroleum cokes used for electrographites are prepared by the delayed coking process; the heavy residue from petroleum fractionators is heated and thermally cracked in a rotating drum at 400 to 450°C. The raw coke from a delayed coker normally contains from 7 to 16 percent volatile matter and various amounts of impurities, depending on the source of the petroleum crude and the processing operations at the refinery.

The domains of embryonic graphite crystals are established during the coking operation. The ultimate graphitizability of the coke is dependent on the size of these domains, the distribution of carbon atoms between turbostratic crystallites, and the relative orientations of adjacent domains. The graphitizability of the coke is, in turn, of major importance in determining the properties of the final graphite. In general, the filler coke has more effect on the properties of the final graphite than does the binder. For this reason, among others, the coke used to produce a given grade of graphite is normally obtained from a single refinery.

Calcination, the next step in the preparation of the coke, is essentially a continuation of the cracking process; by heating the coke to about 1250°C in rotary kilns, the calcining operation removes most of the volatiles and preshrinks the coke, thus minimizing volume changes during subsequent processing of the formed graphite stock. Because of this preshrinkage, graphites prepared from cokes calcined at the higher temperatures tend to have higher densities than those prepared from cokes calcined at the lower temperatures. During calcination, about 25 percent of the weight of the raw coke is lost by the evolution of volatile material, loss of fine particles, and removal of water which was picked up when the coke was hydraulically removed from the coker.

During calcination, the characteristic structure of the crystalline domains develops to a high degree.⁽³⁹⁾ At this stage, differences in morphology of the cokes are easily seen under the optical microscope and in differences in the shape of particles of the ground coke. Toward two ends of the spectrum of particle shapes, one can characterize the blocky, "conventional", coke particles and the more splintery, "needle", coke shapes. The essential difference in morphology, which produces the differences in particle shape, is one of mosaic size, i.e., the dimensions of the region in which the crystallites are closely aligned.⁽⁴⁰⁾ The properties and behavior of the final graphite are strongly dependent on size and shape of the calcined coke particles.⁽⁴¹⁾ Finer grinding tends to fracture the coke particles along shrinkage cracks and at mosaic edges; thus the finer particles are more dense and are of higher anisotropy than the larger particles. The needle cokes, and in general the finer particle sizes, tend to align during forming with their longer axes parallel to the direction of extrusion; thus, they impart increased anisotropy to the finished graphite body. In general, the finer particle sizes produce graphites of higher density, with increases in strength, elastic modulus and thermal conductivity and with reduced thermal expansion and radiation-induced dimensional changes in the direction parallel to the extrusion axis. At the same time, the properties transverse to the extrusion axis change in the opposite direction; the general trends may, however, be obscured by changes in the pitch binder content or in the distribution of the binder.⁽⁴²⁻⁴⁴⁾

Coal tar pitch, which is normally used as the binder for electrographites, is the heavy residue from the distillation of coal tar; coal tar, in turn, is derived from the destructive distillation of bituminous coal to produce metallurgical coke. Coal-tar pitches vary in chemical composition, physical properties and impurity content depending on the source of the coal and on the techniques used in preparing the pitch. Even after graphitization, the binder coke does not develop mosaics beyond a few microns in size, and the binder coke regions are readily distinguished from petroleum coke particles.⁽⁴⁵⁾ Only about half of the weight of the binder pitch remains as

carbon in the finished body; sufficient binder must be used to fill the voids between particles and to allow extrusion of a sound body, but excess binder results in a body of low density.

Up to about 3 wt.% of a petroleum-base lubricating oil is added to the mixture of coke and pitch to reduce friction between the mix and the surface of the extrusion die; the primary requirement is that the oil have low miscibility with the pitch in order that it remain on particle surfaces where lubrication is most important. Although petroleum-base oil does not contribute carbon to the final product, its use allows lower amounts of pitch to be used and, thus, higher densities can be obtained under normal production conditions.

A coal tar pitch having a lower melting point and a lower viscosity than the coal tar pitch used as a binder is normally used as an impregnant to increase the density of nuclear grade graphites. Because of the lower viscosity, the impregnant pitch penetrates more of the cracks and pores in the filler particles than do the binder pitches; at the same time, however, the weight remaining as carbon is lower for the lower viscosity pitches. The composition and properties of the impregnating pitch are subject to the same variations as those of the binder pitch. In general, the increased density is accompanied by an increase in strength, elastic modulus, and volumetric coefficient of thermal expansion (CTE). Other materials⁽⁴⁶⁾ such as petroleum asphalts or thermosetting resins could be used as binder and/or impregnant; however, there has been little experience with the use of these materials under large scale production conditions in the U. S. and they seem to offer little or no advantage except for special applications.⁽⁴⁷⁾

Additives (such as carbon blacks to increase density) or graphitizing aids (such as Fe_2O_3 to promote densification during processing) have been used in some applications. Carbons and graphites containing carbon blacks are discussed, respectively, in the section on special materials and the section on improved nuclear graphites. If graphitizing aids⁽⁴⁸⁻⁵⁰⁾ are added to promote densification during processing or to obtain improved dimensional stability during irradiation,⁽⁵¹⁾ materials are chosen which can be effectively removed during the purification process.

For graphitic materials which have been heated above about 2600°C, the product of the thermal conductivity (K_O) and electrical resistivity (ρ_O), both measured at room temperature, is approximately constant ($K_O \rho_O = 3.1 \times 10^{-4}$ ohm cal/sec deg); the product may vary, however, at other temperatures, for materials which have not been graphitized, and for irradiated graphites.

In general, there are systematic relationships between other physical properties within a series of graphites prepared from the same raw materials and where, perhaps, only one processing variable is changed. These relationships may not hold, however, when several variables are changed simultaneously or when different raw materials are used. In general, the ratio of strength to elastic modulus (i.e., the strain-to-fracture) remains approximately constant. An increase in anisotropy of the body (i.e., an increase in the ratio of properties measured transverse and parallel to the extrusion axis) generally will be produced if the graphitization temperature is increased, the extrusion cross section is reduced, or finer coke particles are used in the filler. Normally, finer coke particles also increase the density and the volumetric CTE. An increase in density can also be produced by multiple impregnations; an increase in density is generally accompanied by an increase in strength and elastic modulus.

RADIATION EFFECTS

Theory

Current theories on the mechanism of radiation-induced changes of dimensions and physical properties are strongly linked, either explicitly or implicitly, to the morphology⁽⁵²⁻⁵⁵⁾ of synthetic graphite. The structure of conventionally processed petroleum coke graphites can be described⁽⁵⁶⁾ as a more or less randomly oriented aggregate of coke particles, each coke particle consisting of highly crystalline regions having more or less the same preferred orientation with respect to the coke particles. These crystalline regions and, on a larger scale, the coke particles are bonded together by a second carbon phase wherein the atoms do not possess the characteristic three dimensional ordering of graphitic crystals. Further complicating even

this simple model are two crack systems which are preferentially oriented parallel to the basal planes of adjacent crystalline regions: 1) The larger crack system, which developed in the coke particles as the crystalline regions developed prior to cool-down from graphitization temperature, is observable in an optical microscope; 2) The smaller (Mrozowski-crack) system, visible in electron micrographs, developed during cool-down from graphitization temperature.⁽⁵⁷⁾ During cool-down, the large differences between the thermal expansion coefficients for the directions parallel and transverse to basal planes of the crystallites result in stresses being generated between adjacent crystalline regions having different orientations in the body. Mrozowski-cracks form where these stresses are sufficiently high; at other positions internal stresses remain and can affect the initial dimensional changes during irradiation.

Mathematical expressions for the "Single Phase Model," which is based on the primary assumption that the aggregate behaves as if it were composed of only unrestrained crystallites, were first derived by Simmons;⁽⁵⁸⁾ these equations can be written in the general form:

$$A_X \equiv \frac{\alpha_X - \alpha_a}{\alpha_c - \alpha_a} \quad (1)$$

$$dL_X = A_X (dX_c - dX_a) + dX_a \quad (2)$$

A_X is an empirical constant, defined by equation 1, which depends on the type of graphite, the direction in the graphite body, and on the prior treatment of the graphite. α_X is the thermal expansion coefficient in the x-direction of the polycrystalline body, α_c and α_a are the lattice expansion coefficients transverse and parallel, respectively, to the basal planes of the component crystallites, dL_X is the rate of length change per unit dimension of the polycrystalline body in the x-direction as a function of neutron fluence and irradiation temperature, and dX_c and dX_a are the corresponding rates of dimensional change per unit dimension for the graphite crystallites transverse and parallel to the basal planes, respectively.

Starting with the single-crystal averaging model of Bacon,⁽⁵⁹⁾ Jenkins⁽⁶⁰⁾ and Morgan⁽⁶¹⁾ have independently shown that Simmons empirical constant A_x can be expressed as the complex product of the crystallite orientation function, which is measurable by x-ray diffraction techniques, and an accommodation factor, γ_x , which is related to the microcrack structure within the aggregate.

Other attempts to extend the work of Bacon have been reported previously by Sutton and Howard⁽⁶²⁾ and by Price and Bokros.⁽⁶³⁾ In both cases, however, arbitrary and erroneous assumptions, which invalidate⁽⁶⁴⁻⁶⁶⁾ the relationships used by these authors, were made in regard to the interrelationships between accommodation factors. The single phase relationships have been used with some success to correlate dimensional changes on well graphitized materials over a limited range of irradiation temperatures and fluences; however, the effects of internal stresses and changes in the intercrystalline regions of the aggregate become increasingly important for irradiations at higher temperatures, under applied stress, and for less well graphitized materials.⁽⁶⁷⁻⁷²⁾

Dimensional Changes

The radiation-induced dimensional change behavior of petroleum coke-based nuclear graphites irradiated at temperatures above about 300°C can be summarized^(11-26, 73-78) as follows:

1. At very low fluences the relaxation of internal stresses, which were introduced during cool-down from graphitization temperature and were not relieved by generation of the microcrack system, generally results in a slight expansion of the graphite samples.
2. During irradiation, the component crystallites shrink in the directions parallel to their basal planes and expand in the direction perpendicular to the basal planes;^(79,80) the ratio of the dimensional change rates, $dX_c/-dX_a$, decreases from about 3 at 400°C and approaches 2 at temperatures of 1000°C or higher. Thus, at the higher temperatures the crystallites undergo little change in volume, the primary change being in crystal shape.

3. The crystallite contraction, dX_a , is reflected in a contraction of the aggregate while most of the expansion, dX_c , is absorbed by closure of the crack systems oriented parallel to the crystallite basal planes.
4. At higher fluences, the oriented crack system is closed and internal stresses are generated by the continued crystallite expansion; this is first reflected in a cessation of contraction and the beginning of expansion in the direction transverse to the original extrusion direction of the aggregate. This phenomenon is referred to as "turnaround".
5. In the direction parallel to the extrusion direction, contraction continues to much higher fluences due to the displacement of material and reorientation of crystallites which occur under the influence of the newly generated internal stresses.

Figures 1 and 2 show the normal sampling schemes for extruded graphites and Figures 3 and 4 show typical dimensional changes as a function of irradiation temperature and fluence for samples of NC8 graphite cut transverse, ($\perp$), and parallel, ($\parallel$), respectively, to the original direction of extrusion. The designation NC8 refers to samples cut from a particular bar of graphite which was produced for the Experimental Gas-Cooled Reactor; additional information on NC8, and other graphites referred to in the following sections, is listed in Table I. Figure 5 shows the volume changes derived from the dimensional changes shown in Figures 3 and 4. The general trends can be summarized as follows:

1. In the temperature range from 400°C to about 800°C,⁽¹⁶⁾ contraction rates in both directions are reduced as the temperature is increased.
2. In the temperature range from about 800°C to about 1200°C,⁽¹⁷⁾ the initial contraction rates again increase with increasing temperature; however, the transverse samples go through turnaround at lower fluences as the irradiation temperature is increased and rapidly expand thereafter. The shape of the volume change curves reflect the same general features as those of the transverse length changes.

TABLE I
DESCRIPTION OF GRAPHITES

<u>Graphite Type</u>	<u>Manufacturer</u>	<u>Extrusion Size, in.</u>	<u>Additive</u>	<u>Description</u> ^(a)	<u>Density (gm/cm³)</u>	<u>Coefficient of Thermal Expansion (25-425°C)</u>		<u>Young's Modulus psi x 10⁻⁶</u>	
						<u>Transverse</u>	<u>Parallel</u>	<u>Transverse</u>	<u>Parallel</u>
NC8	Union Carbide	17-1/2x17-1/2	None	Produced for the Experimental Gas-Cooled Reactor	1.72	3.3	1.7	0.83	1.5
9567	Speer Carbon	18 (diam.)	~1% FeO	Experimental Graphite	1.71	3.6	1.4	0.90	1.7
H327A	Great Lakes	12-3/4 (diam.)	none	Developmental Graphite	1.78	3.4	1.2	0.89	2.2
H327	Great Lakes	17-1/2 (diam.)	--	Produced for the Fort Saint Vrain HTGR	1.78	2.6 ^(b)	0.9 ^(b)	--	--

(a) Calcined petroleum needle-coke filler, coal tar pitch binder, extruded, graphitized to 2800°C.

(b) Calculated from mean CTE (22-1000°C) reported by Cobb (Ref. 82).

3. Above about 1200°C⁽⁸¹⁾ the fluence range in which turnaround occurs cannot be defined as distinctly as at the lower temperatures; also, the radiation-induced changes as a function of temperature appear to be even more dependent on graphite morphology than they were at the lower temperatures.

In Figures 6 and 7, the dimensional changes of two other needle coke graphites (H327A and 9567) are compared with those of NC8 graphite at 900 $\pm$ 50°C and 1175 $\pm$ 25°C. As can be seen from the data shown in these Figures, dimensional changes are not comparable on the basis of a simple ratio between graphite types. It should also be emphasized that the data shown in Figures 6 and 7 were from samples which had identical irradiation histories; thus, the comparisons between graphite types can be made directly and are not effected by uncertainties in the determination of irradiation temperature or neutron fluence.

Figures 8 and 9 show typical dimensional change data on H327A graphite which is the designation applied to a preproduction extrusion of H327 graphite. H327 graphite was used for the core blocks in the Fort St. Vrain reactor.

It should be noted that engineering-type curves of predicted dimensional change versus irradiation temperature have been previously published for the Fort St. Vrain fuel blocks;^(10,82) however, a considerable amount of additional data have become available since publication of these curves and the most reliable data (including these shown in Figures 6 and 7) indicate the need for substantial revisions in the earlier predictions. A comprehensive program to compile and re-evaluate irradiation data on H327 graphite is currently in progress.⁽⁸³⁾

Size Effect

Because of the limited size of most irradiation facilities and the cost of irradiation space, studies of radiation-induced changes of graphite are normally conducted on small samples cut from production-size bars, but

not necessarily bars from a production lot. There are variations in physical properties from place to place within a bar and variations from bar to bar even within a single production lot of materials. Thus, one can identify three primary sources of uncertainty in attempting to apply data from irradiation damage studies to a particular position in an operating power reactor. These are:

1. The particular bars (or bar) from which the samples were cut may not be typical of production material.
2. The samples selected are not necessarily typical of material within that bar.
3. The measured properties and/or changes in properties may be effected by sample size or dimensions.

Additional complications are introduced by differences in neutron spectra, neutron flux intensities, and temperature variations which exist as a function of both position and time within an operating power reactor; these effects and their possible consequences are discussed in more detail in later sections of this report.

Variations from bar to bar and for positions within the bars⁽⁸⁴⁾ can be, and normally have been, established through the withdrawal and testing of bars from individual production lots of material. It is well known that certain properties such as tensile strength are highly dependent on sample size and shape for brittle materials like graphite,^(85,86) but the dependence of radiation-induced changes on sample size and/or shape has not been well determined. Perhaps the most important of these changes is the dependence of dimensional change rates on sample size.

In 1964, Nightingale and Woodruff⁽⁸⁷⁾ reported that the dimensional changes measured in the transverse direction on several large, almost full production-size, bars of graphite were about twice the changes measured on small-sized (0.5 inch diameter) irradiation samples.

Horner et al.⁽⁸⁸⁾ concluded that a corresponding enhancement in contraction rate was not applicable to parallel samples of PGA type graphite irradiated at lower temperatures; these results must, however, be tempered by the fact that the large samples and small samples were not from identical material nor were they irradiated in the same reactor.

In addition, Cobb⁽⁸⁹⁾ concluded that the dimensional changes measured at low fluence on an AGOT grade graphite reflector element from the Peach Bottom Reactor were in good agreement with predicted changes; however, considering the low fluences and the gradients in both temperature and flux with position in this element, the results do not eliminate the possibility of an enhanced dimensional change rate.

Since the original observations were reported, additional data^(90,91) have been accumulated which tend to reinforce them. Although technical questions remain unanswered, the general conclusion can be summarized⁽⁹²⁾ as follows:

1. Several bars of several types of graphite yield comparable results; thus, bar to bar variations can be effectively ruled out as the cause of the observed differences.
2. Differences of as much as 20% may be attributed to a bias introduced by the selection of samples from the central portions of the bars.
3. As much as 25% of the enhanced contraction might be attributable to inadequate temperature control for the large bars. It has been shown that even a short irradiation at low temperatures can significantly enhance the subsequent contraction rate. This "cold-seeding" effect, however, becomes less important at higher fluences.
4. It has been postulated^(93,94) that the primary cause of the enhancement of contraction rate can be attributed to internal stresses generated in the samples and the preferential relief of these stresses near the sample surfaces. If this is the primary mechanism, one can conclude that the

increase in contraction rate would be dependent on: 1) manufacturing parameters (such as particle shape and size, binder content and extrusion size) which affect the relative crystallite orientations and morphology of the graphite bars, 2) the temperature of irradiation, and 3) sample orientation (with contraction in the transverse direction being affected to a greater extent than the contraction parallel to the direction of extrusion).

Radiation Creep

In an operating reactor, especially one having blocks of large size containing fueled regions, large gradients in temperature and neutron flux can exist within each block. Since the dimensional change rates are strongly dependent on temperature and fast neutron flux, internal stresses will be generated within the blocks due to the differences in dimensional change rates. In the absence of a stress relief mechanism, these differential stresses could exceed the rupture strength of the graphite and cause massive fracturing of the blocks. Relief of these stresses through radiation-induced creep is, thus, an important factor in HTGR design.⁽⁹⁵⁻⁹⁷⁾

Thermally induced creep of graphite does not occur at significant rates below about 2000°C, but radiation-induced creep occurs at significant rates at all temperatures investigated. Creep takes place in two stages; the first (or primary creep) stage, which is approximately a logarithmic function of fluence and approximately proportional to the initial elastic strain, is a reversible process and rapidly goes to completion at low fluences. The secondary or steady-state creep is an irreversible process which is a linear function of fluence and applied stress. Thus, an equation for the creep strain, ϵ , can be written in the form:

$$\epsilon = A\sigma \ln(1 + B\phi) + C\sigma\phi \quad (3)$$

where A and B are constants, σ is the applied stress, ϕ is the neutron fluence, and C is the steady-state creep coefficient. The subject of creep rates has been recently reviewed by Kelly and Brocklehurst⁽⁹⁸⁾ and by Platonov.⁽⁹⁹⁾ Although the theoretical basis for radiation-induced creep

is still not resolved, the authors of both reviews agree that an inverse relationship exists between the creep coefficient and Young's modulus (or strength, which is proportional to Young's modulus). Figure 10 shows typical values of the creep rate coefficients as a function of temperature.⁽⁹⁹⁻¹⁰¹⁾

Recent results by Gray,⁽¹⁰¹⁾ for samples irradiated under compressive stress to higher fluences than have been investigated previously, confirm that creep rates are an inverse function of elastic modulus, and indicate that:

1. Turnaround may occur at much lower fluences than for unstressed samples;
2. At turnaround, the creep coefficients which are constant at lower fluences, may actually become negative rather than just becoming zero;
3. Creep strains, up to about 5% at turnaround, are accommodated at approximately constant volume.

In light of these results, it is concluded that:

1. A fairly sophisticated, three dimensional viscoelastic model is required to calculate dimensional change rates, stress generation, and creep rates in a realistic manner for HTGR fuel block assemblies because of the three dimensional interdependency of these properties;
2. The ratio of the internal stress to the breaking strength will be relatively insensitive to changes in the strength, elastic modulus, or creep rate because the strength is proportional to the elastic modulus and the creep rate is an inverse function of the elastic modulus; and
3. There is a definite limit to the creep strain which can be accommodated in compression and that if this limit is reached, rapid increases in internal stresses and physical deterioration of the graphite component may follow immediately.

Physical Properties

Physical properties of importance to HTGR design are thermal expansion, strength, elastic modulus, and thermal conductivity. The general interrelationships between these properties at room temperature and their dependence on manufacturing variables has been discussed in the previous section on manufacturing processes. The dependence of the properties on temperature, their radiation-induced changes and their importance to HTGR design are discussed below.

Standard procedures for the measurement of the physical properties of graphite and carbons are contained in Part 13 of the ASTM Annual Book of Standards.⁽¹⁰²⁾ The physical properties of graphite have recently been reviewed by Reynolds⁽¹⁰³⁾ and a, soon-to-be-released, review by Kelly and Taylor⁽¹⁰⁴⁾ covers the thermal properties of graphite. Cobb et al.⁽¹⁰⁵⁾ have reported data on the physical properties of production-grade H-327 graphite; other reviews or publications of data on specific properties or on other graphites are noted below.

Thermal expansion and changes in the coefficient of thermal expansion are important from two standpoints:

1. Radiation-induced changes in dimensions are measured at room temperature; but, it is the dimensions at irradiation temperature which affect reactor operation.
2. During a reactor shutdown, elimination of the large thermal gradients, which existed during operation, will result in generation of "thermal" stresses within the blocks; depending on design and operating conditions, these "thermal" stresses either add to, or counteract, the "quasi-equilibrated" stresses which existed during operation.

The stresses generated will, obviously, depend on temperature gradients, the thermal expansion coefficients, and the elastic moduli of the block. However, because of the proportionality between elastic modulus and strength, the likelihood of fracture is primarily determined by the thermal expansion coefficients and temperature gradients.

Thermal expansion coefficients (CTE) of nuclear graphites are normally measured and reported as the mean coefficient between two fixed temperatures (i.e., 25 to 425°C). Morgan⁽¹⁰⁶⁾ has recently reviewed the data on thermal expansion of graphite crystals as a function of temperature and fitted the lattice expansion data to the theoretical equations derived by Riley.⁽¹⁰⁷⁾ Over the range of temperatures of interest for HTGR's, these lattice expansion data may be used with the single-phase^(58,61) equations to interpolate or extrapolate thermal expansion data on unirradiated polycrystalline graphites to other temperatures.

In general the changes in CTE follow the same trends as the changes in length, first decreasing with fluence and then increasing after turnaround. Prior to turnaround, the single phase equations provide a reasonable fit to the thermal expansion data taken as a function of temperature below the irradiation temperature; however, after turnaround, the closure of the crack system at irradiation temperature and its partial regeneration at lower temperatures causes the thermal expansion to increase too rapidly with temperature. In other words, the accommodation factor, γ , becomes a function of temperature instead of being a constant. This behavior is illustrated by the thermal expansion data⁽¹⁰⁸⁾ on samples of H327A graphite, as shown in Figures 11 and 12. As can be seen from Figure 11, the thermal expansion ($\Delta l/l$) of the unirradiated samples can be described quite well using a "single-phase equation"⁽⁶¹⁾ of the form:

$$(\Delta l/l)_X = A_X(\alpha_c - \alpha_a)\Delta T - \alpha_a \Delta T \quad (4)$$

where $A_X = K_X \gamma_X$, K_X is a crystallite orientation parameter, measured by the method of Bacon⁽⁵⁹⁾ γ_X , the "accommodation coefficient" is a constant, and $\alpha_c \Delta T$ and $\alpha_a \Delta T$ are the crystal lattice thermal expansions measured transverse and parallel, respectively, to the crystal basal planes over the temperature range, ΔT , from 25°C to the temperature of the measurement.

By referring to Figures 3 through 9 incl., one can see that the transverse samples (66-9-13, -18, and -35), whose thermal expansion behavior departs most strongly from the "single-phase" behavior, have passed through turnaround and are expanding; the parallel sample 66-9-213, whose thermal expansion behavior still follows the single-phase relationship, is still contracting rapidly and the remaining two samples, whose thermal expansions deviate only slightly from single-phase behavior, are approximately at turnaround.

The departure from single-phase behavior is seen more clearly in Figure 12, where A_x , calculated by use of Equation 1, is plotted versus temperature for these samples.

It has also been shown^(109,110) that the CTE and Young's Modulus of unirradiated samples is changed by an appreciable amount by the application of stress. Such an effect is also expected during irradiation.

Blakslee et al.⁽¹¹¹⁾ have recently redetermined the elastic constants of graphite crystals and Seldin and Nezbeda⁽¹¹²⁾ have published a similar study of the elastic constants of irradiated crystals. Reviews by Tsuzuku and Saito⁽¹¹³⁾ and by Taylor and Kline⁽¹¹⁴⁾ have covered the internal friction and the changes in dynamic mechanical properties of graphite.

During irradiation both the strength and elastic moduli increase to new "quasi-saturated" values, the percentage increase generally being inversely dependent on irradiation temperature. Values of Young's modulus, measured by sonic resonance techniques, have been reported by Helm⁽¹⁶⁾ and by Morgan and Gray.⁽¹⁷⁾ Very little data exist on strengths of highly irradiated samples but it appears that the change in strength may parallel the change in modulus (i.e., the elastic strain-to-fracture remains constant) at least until turnaround.

Since graphite is a brittle material with a large number of anisotropically oriented flaws (cracks), strengths measured on small samples are highly dependent on flaw sizes and, thus, on sample size and shape. There is a fairly wide distribution in the measured strengths,^(115,116) as is predicted from Weibull Statistical Theory, and there is some indication that the distribution of strengths may increase during irradiation.⁽¹¹⁷⁾ If this is the case, it would, at least partially, cancel any benefits gained from the increase in strength. A further complication is introduced by the fact that measurements are normally obtained from uniaxial tests, while the stresses and strains generated in the reactor graphite blocks will be multi-axial. With proper treatment, however, uniaxial data can be used to predict behavior under multi-axial loading.⁽¹¹⁸⁻¹²⁰⁾

The thermal conductivity of polycrystalline graphite has been reviewed by Kelly⁽¹²¹⁾ and the thermal conductivity of graphite single crystals has been covered by Kelly and Gilchrist⁽¹²²⁾ and by Tanaka and Suzuki.⁽¹²³⁾ Additional recent data on unirradiated polycrystalline graphites has been published by Wagner and Dauelsberg⁽¹²⁴⁾ and Lutcov et al.⁽¹²⁵⁾ Taylor et al.⁽¹²⁶⁾ have reviewed the effect of neutron irradiation on thermal conductivity.

The room-temperature thermal conductivity of graphite decreases rapidly during irradiation, but the fractional change is smaller near the irradiation temperature than at room temperature. A report by Bell et al.⁽²⁴⁾ contains an extensive tabulation of the changes in room-temperature thermal conductivity $(\frac{K_0}{K} - 1)$ and stored energy (E) at irradiation temperatures up to 350°C where K_0 is the thermal conductivity of an unirradiated sample and K is the thermal conductivity after irradiation, both measured at room temperature. The general relationship $E = 6.25 \text{ cal/gm} (\frac{K_0}{K} - 1)$ was found to be independent of temperature over the range of irradiation temperatures (150° to 350°C) investigated. Helm⁽¹⁶⁾ tabulates some of the data obtained by Baker⁽¹²⁷⁾ on thermal conductivities as a function of temperature for both irradiated and unirradiated samples. Using the above relationship between changes in thermal conductivity and stored energy, it is estimated

that the maximum accumulation of stored energy in the graphite of the current generation of HTGR's would not exceed 50 cal/gm; instantaneous release of this amount of stored energy would increase graphite temperatures by about 150°C. Other methods⁽²¹⁾ predict even lower values for the maximum stored energy accumulation.

Engle and Koyama⁽¹²⁸⁾ have reviewed the thermal conductivity data and concluded that the changes measured at the irradiation temperature are a linear function of the irradiation temperature, with the conductivity remaining unaffected by irradiation above about 1400°C. Although this conclusion may be sufficient within a narrow range of fluences, it would seem to be a considerable over-simplification to assume that it remains valid over a range of fluences, especially near turnaround.

Changes in many physical properties are produced by oxidation of graphite at a rate which is much larger than the percentage change in density;⁽¹²⁹⁻¹³¹⁾ more over, Krefeld et al.⁽¹³²⁾ have recently shown that tensile stresses can accelerate the oxidation rate. It appears that the acceleration of oxidation rate due to stress may, in turn, accelerate the degradation of physical properties as a function of oxidation.

Studies on the erosion of graphite have normally been conducted under conditions which are characteristic of those encountered in aerospace applications⁽¹³³⁾ but, which are of little interest for HTGR design. It has been shown,⁽¹³⁴⁾ however, that in the absence of preferential oxidation of the binder material (which would tend to loosen particles at the surfaces), the erosive effect of hot gas is negligible.

III. CHEMICAL REACTIONS OF GRAPHITE

In the present generation of high-temperature gas cooled reactors, helium passes through the core at pressures up to 47 atmospheres carrying the heat from the core to the high pressure steam heat exchangers. Current system designs yield helium temperatures up to 800°C with graphite surface temperatures in some instances reaching 1100°C. These conditions combined with the ionizing environment of the nuclear reactor place rigid requirements on the purity of the helium coolant. Yet the potential for contaminating the helium is always present. Before the initial startup and during any subsequent opening of the primary circuit, the large quantities of graphite tend to adsorb substantial volumes of water vapor, oxygen, and hydrogen which are released to the coolant gas as the temperature is increased. The main source of continuous contamination of the helium is leakage of water through the heat exchanger tubes. Other potential impurity sources include 1) leaks of lubricating oils, and 2) steam side corrosion followed by diffusion of the resulting hydrogen through the heat exchanger tubes.⁽³⁰⁾

These impurities in the helium coolant undergo a variety of reactions in the primary circuit due to the ionizing radiation as well as the high temperatures. The steady-state level of impurities is controlled by a rather complicated combination of the inleakage and outgassing rates, the reactivity of the graphite and metal surfaces, and the purification rate.

Everett, et al.⁽²⁹⁾ have summarized the reactions of importance to graphite corrosion and carbon deposition in a diagram on the following page.

The literature is replete with information about the thermally induced reactions of various gases with carbons and graphite. However, very little information has been published concerning the effect of radiation on the reactions of interest. In spite of the lack of information many important conclusions can be and have been drawn to enable adequate predictions of coolant-core interactions in the HTGR. The basic reactivity data and the conclusions drawn are summarized in the following paragraphs.

CORE

Reactions in the core at graphite temperatures up to 1100°C and gas temperatures up to 800°C

Purified He

In-leakage:
H₂O, (O₂, N₂, CO₂)
Outgassing:
H₂O, CO, H₂, CH₄, CO₂

Main Coolant Flow
47 atm

STEAM GENERATOR

Reactions at heat exchangers (T:350 to 750°C) and other hot metal surfaces

Main Coolant Flow
47 atm

Purification
Flow

PURIFICATION SYSTEM

He plus H₂O, O₂, N₂, CO₂, CO, H₂, CH₄,
(CN)₂, HCN, and fission products

BNWL-1687

THERMAL REACTIONS

The high temperature reaction of carbon with gaseous oxidants, hydrogen and in some cases even with nitrogen, presents a major threat to the graphite core of a HTGR. Thus, these impurities must be controlled at a low level. The establishment of realistic impurity levels requires a knowledge of the kinetics of the applicable reactions under HTGR conditions to evaluate the extent to which reactions will occur. The following is a review of the current knowledge of the kinetics of the most important reactions. In some cases thermodynamic or equilibrium considerations may limit the reaction, but, in general, kinetics will control the process.

Carbon-Oxygen Reaction

The design of the HTGR essentially eliminates the potential for oxygen ingress into the reactor core, so the graphite-oxygen reaction has been given only minor attention. On the other hand, adsorbed oxygen may be released from the reactor components during heat up and, under certain accident conditions, oxygen may also be admitted to the core from the atmosphere. Therefore, the kinetics are discussed in this review.

The reactivity of graphite to oxygen is such that the purification system cannot effectively compete with the core. Thus it can be assumed that the oxygen will be rapidly converted to carbon monoxide and carbon dioxide. Therefore, carbon removal rapidly occurs and is accompanied by a temperature increase from the heats of the reaction which are 27 kcal/mole for CO production and 94 for CO₂.

The kinetics of the carbon-oxygen reaction have been studied thoroughly and have been described in a review by Walker et al.⁽²⁷⁾ The reaction proceeds with the production of CO and CO₂, both of which are considered to be primary products. The CO/CO₂ ratio increases exponentially as the temperature increases. Most investigators have reported that the reaction is first order in oxygen. However, two groups^(136,137) have reported zero order for the reaction at oxygen pressure below about 0.01 atmospheres.

The activation energy of the carbon-oxygen reaction has been reported by various authors (see ref. 27) at values between 17 and 100 Kcal/mole-degree but the true value for the chemically controlled rate is very likely between 40 and 58 Kcal/mole-degree. With this amount of variation in rates, it is impossible to rely on a single expression for the rate of reaction under a variety of conditions. Rather, measurements should be made with the graphite of interest under conditions close to those of the operating system. On the other hand, it is useful to make estimates, and using the appropriate degree of conservatism, these estimates may be sufficient for design purposes. Gulbransen and co-workers⁽¹³⁸⁾ have measured the rate of reaction of oxygen with spectroscopic carbon in the temperature range 600-1500°C. Using their data we have derived the following rate expressions:

$$\frac{-dc}{dt} \text{ (g/cm}^2\text{-sec)} = 5 \times 10^2 e^{-39,000/RT} (.06 + 11.9 P_{O_2}); T < 800^\circ\text{C}$$

$$\frac{-dc}{dt} \text{ (g/cm}^2\text{-sec)} = 2.2 \times 10^{-7} e^{-3600/RT} P_{O_2}^{0.32}; T > 800^\circ\text{C}.$$

It should be noted that some treatments of data⁽¹³⁹⁾ tend to predict a rate nearly four orders of magnitude higher than predicted by the above expressions. However, in the absence of significant catalyzed reactions, the expressions given appear to apply reasonably well to HTGR conditions.

If a total loss of coolant occurred, the graphite temperatures in the HTGR core may substantially exceed 1100°C. Under these conditions the oxidation rate of graphite could not be adequately predicted by an extrapolation of the low temperature data. In fact Eyring and his students have shown⁽¹⁴⁰⁾ that the rate of reaction goes through a maximum in the range of temperatures from 1000 to 1300°C and then decreases as the temperature continues to increase.

All of the above rate data assume a chemically controlled rate. Under most HTGR conditions, however, the reactions will be limited by the diffusion rate of the gas, as discussed in a later section of the review.

Carbon-Carbon Dioxide Reaction

Although there is little potential for carbon dioxide to leak into the reactor vessels in significant quantities, it is nevertheless an important impurity since it is generated by other reactions occurring within the reactor core. A considerable volume of literature⁽²⁷⁾ has been reported on the mechanism of the reaction of CO₂ with various carbons to form CO. While it is generally agreed that the rate of the reaction can be expressed as

$$\frac{-dc}{dt} = \frac{k_1 P_{CO_2}}{1 + k_2 P_{CO} + k_3 P_{CO_2}},$$

there is considerable disagreement as to the value and form of the various constants. In fact, most workers have studied the reaction to only a limited extent and thus, have reported only the overall rates and temperature coefficients rather than the individual rate constants.

In the absence of specific rate data at low pressure in a helium atmosphere, one must extrapolate other literature values to obtain a prediction for the rate of carbon removal due to the reaction with CO₂. To enable this extrapolation, Giberson⁽¹⁴¹⁾ has suggested the following rate constants for the reaction of CO₂ with nuclear graphites:

$$k_1 = 1.69 \times 10^6 e^{-66,800/RT} \text{ atm}^{-1} \text{ sec}^{-2}$$

$$k_2 = 1.15 \times 10^{-4} e^{+29,500/RT} \text{ atm}^{-1}$$

$$k_3 = 2.66 \text{ atm}^{-1}$$

Carbon-Water Vapor Reaction

By far the most important coolant impurity in the core of an HTGR is water vapor because of the potential for leakage, slowly but continuously, through the heat exchanger tubes into the primary circuit. As the water enters the helium it reacts with the hot graphite producing CO and H₂. The impurity levels are thus largely determined by the inleakage rate of water, the reactivity of the hot core, and the rate of removal of impurities in the purification system.

The rate expression for the reaction of water vapor with carbon and graphite is reported⁽²⁷⁾ to be completely analogous to that of the carbon-carbon dioxide reaction.

$$\frac{-dc}{dt} = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2} + k_3 P_{H_2O}}$$

Thus, the order of the reaction with respect to H_2O varies from zero to one depending upon temperature, concentration, and the type of carbon. There is wide variation in the absolute values of the rate constants, but it is generally agreed that k_2 and k_3 decrease exponentially with temperature, thus yielding a reaction first order in water vapor at sufficiently high temperatures.

Giberson and Walker⁽¹⁴²⁾ studied the effects of hydrogen on the reaction and reported a better fit of the data if the H_2 inhibition term is 0.5 order. Thus the following expression was recommended:

$$\frac{-dc}{dt} = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2}^{1/2} + k_3 P_{H_2O}}$$

The same authors later reported⁽¹⁴¹⁾ the following values for the rate constants:

$$k_1 = 26.5 e^{-32,700/RT} \text{ atm}^{-1} \text{ sec}^{-1}$$

$$k_2 = 3.42 \times 10^{-10} e^{+60,800/RT} \text{ atm}^{-1/2}$$

$$k_3 = 4.95 \times 10^{-16} e^{+79,300/RT} \text{ atm}^{-1}$$

Carbon-Hydrogen Reaction

Some kinetic data exist on the carbon-hydrogen reactions but under conditions much different than those expected in a HTGR. Zielke and Gorin⁽¹⁴³⁾ studied the reaction and suggested the rate expression:

$$\frac{-dc}{dt} = \frac{A(P_{H_2})^2}{1 + B(P_{H_2})}$$

Corney and Thomas⁽¹⁴⁴⁾ studied the reaction of PGA graphite with hydrogen and reported data which we have used to calculate the following expression:

$$\frac{-dc}{dt} = 1.7 \times 10^9 e^{-65,000/RT} (P_{H_2})^2$$

This expression is derived from the Zielke and Gorin expression at low hydrogen pressures where the term $BP_{H_2} \ll 1$.

From a practical point of view, however, the kinetics of the H_2 -carbon reaction is of little importance in a helium cooled reactor because of thermodynamic limitations. The equilibrium constant for the reaction is defined as $[CH_4]/[H_2]^2$ and has a value which varies from about 1×10^2 at $300^\circ C$ to 2.5×10^{-3} at $1200^\circ C$.⁽¹³⁵⁾ Under normal operating conditions P_{H_2} would rarely exceed 10^{-4} atm and thus the P_{CH_4} concentration would be undetectable. It is difficult to conceive of any condition where the H_2 pressure would become sufficiently high to produce a significant amount of methane. Rather it is more likely that methane would tend to decompose to yield hydrogen and carbon.

Carbon-Nitrogen Reaction

Carbon- N_2 reactions, with the formation of CN and CN_2 , have been reported but would not occur in HTGR because the equilibrium constants have extremely low values at temperatures below $2700^\circ C$.⁽²⁸⁾

DIFFUSION LIMITATIONS

Thus far in this document the kinetic data listed have been applicable to conditions where the reaction rates were chemically controlled (i.e., diffusion of the gases was rapid compared to the rate of the chemical reaction). Under the conditions of temperature and flow in helium-cooled reactors, these conditions no longer apply and corrections must be made to the chemically controlled rate because of the diffusion limitations. Walker⁽²⁷⁾ reviews the three steps which are involved in heterogeneous reactions; namely, 1) mass transfer of reacting gas and products across a relatively stagnant gas film between the exterior surface of the solid and the main gas stream, 2) mass transport of the reacting gas from the exterior surface to an active site beneath the surface and mass transport of the products in the opposite direction, and 3) chemisorption of reactants followed by rearrangement of the adsorbed species and desorption of the products. These three steps produce three distinctly different rate zones which are generally referred to as Zone 1, the chemically controlled zone; Zone 2, the impure diffusion zone; and Zone 3, the stagnant film zone.

Everett, Kinsey, and Romberg⁽²⁹⁾ have thoroughly reviewed the diffusion effects as they relate to the geometry and operating conditions of HTGR's. They concluded that, for a system of 40 atmospheres helium pressure, the O_2 -graphite reaction will be mass-transfer limited at temperatures above 800°C for turbulent flow. (For laminar flows mass-transfer limitation should occur at even lower temperatures.) For the CO_2 -graphite and H_2O -graphite reactions, with their lower inherent reactivity, mass-transfer limitation does not occur until the temperature exceeds 1400°C. Thus, only in rare instances will it be necessary to consider mass-transfer limitations (Zone 3). On the other hand, the rates of impurity reactions with the carbon in HTGR are generally limited by impure diffusion (Zone 2).

The theoretical treatment of in-pore diffusion has received the attention of several workers as reviewed by Walker.⁽²⁷⁾ Recently, Malinauskas⁽¹⁴⁵⁾ has studied the reaction of graphite with water vapor limiting the gas flow to only one side of the graphite, thus enabling a more simplified diffusion model. By this approach he was able to demonstrate reasonable agreement between the theory and the experimental data.

Kinsey and Harper⁽¹⁴⁶⁾ defined the diffusion limited rate constant, k_{DL} , as follows:

$$k_{DL} = \sqrt{k_1 \cdot D_{eff}}$$

where k_1 represents the true chemical rate constant and D_{eff} is the effective diffusion coefficient of the reactive gas into the graphite. They concluded that the concentration ratio, $R(x)$, of the gas at a depth x below the graphite surface to that at the surface was

$$R(x) = \exp\left(-x\sqrt{\frac{k_1}{D_{eff}}}\right)$$

Thus, for a fuel tube 5 mm thick, typical values of $R(x)$ for the inner surface of the tube were listed as:

~ 0.1 at 800°C 50 atm He

$\sim 10^{-5}$ at 900°C 50 atm He

In Giberson's⁽¹⁴⁷⁾ treatment of the HTGR coolant graphite system, he defined the diffusion limited rate as

$$R_{DL} = \eta R_h$$

where R_h is the homogeneous or chemically controlled rate and η is the diffusion correction which depends on the diffusion coefficient (D_{eff}), the gas pressure, the temperature, and the graphite geometry. D_{eff} was further defined as

$$D_{\text{eff}} = mD_{12}$$

where D_{12} is the mutual diffusion coefficient and m is a constant related to the tortuosity and porosity of the graphite. For nuclear graphites, values of m ranging from 4×10^{-4} to 1×10^{-2} have been reported. Giberson has normally used a value of 1×10^{-3} for his HTGR analyses.

RADIATION INDUCED REACTIONS

In the high radiation field of nuclear reactors, radiation induced reactions often contribute significantly to the chemistry of the reactor core. In fact studies performed in the United Kingdom⁽¹⁴⁸⁾ on CO_2 cooled-graphite moderated reactors have shown that the corrosion of the graphite by CO_2 is largely due to radiolytic processes. Extrapolation of these data to the He-cooled reactors with the low partial pressures of CO_2 led to a prediction that the radiolysis reaction would not be significant in the HTGR. However, when confirmatory tests were conducted, the results showed that radiation greatly enhanced the corrosion rate of graphite by low concentrations of CO_2 in helium.⁽²⁹⁾ The unexpected and rather startling results of the initial experiments led to an extensive study by the Dragon Project. This study included the design and construction of the Inpile Carbon Transport Loop at Mol, Belgium, as well as an experiment conducted for the Dragon Project by Nencini at Milan, Italy where the gases were exposed to x-rays.

The results of the inpile experiments showed substantial enhancement in reaction rate of both H_2O and CO_2 with graphite at temperatures below 800°C with some enhancement evident even at 900°C . Tests which included a variety of gas mixtures of CO_2 , H_2O , CO , H_2 , and CH_4 were run at low concentration (ppm levels) of impurity in helium at ten atmospheres pressure. It was evident from the results that some of the energy used in exciting helium was effectively transferred to the impurities leading to reactions of the excited impurities with the graphite. The results of the inpile experiments along with x-ray studies led the Dragon staff to conclude that "in a Dragon-type power reactor with a power density of 8 MW/m^3 , the maximum corrosion rate due to radiation effects alone would be of the order of $10^{-3} \text{ mg/cm}^2\text{-hour}$, which corresponds roughly to the thermal rate at 900°C with a

total impurity content of 200 μ atm in He at 40 atm" (about 5 ppm impurity).⁽²⁹⁾ The enhancement of graphite corrosion by radiation in a high-temperature reactor is largely beneficial because it tends to spread the corrosion to a larger area of graphite and also tends to limit the reaction more to the geometrical surface rather than to the interior pores of the graphite.

The Dragon inpile experiment was designed as an applied study to determine the effect of radiation upon the corrosion of graphite under somewhat typical HTGR conditions. Although this work led to a good deal of information about the radiolysis reactions of interest to HTGR, its applied nature made it difficult to interpret in terms of fundamental reaction parameters and also difficult to extrapolate to other reactor conditions.

During this same period a more fundamental approach to the study of radiolysis reactions in helium was conducted in the U. S. by Tingey⁽¹⁴⁹⁾ and his associates. The radiolytic rate for the CO_2 -graphite reaction had already been reported⁽¹⁴⁸⁾ to have a value of 2.0 to 2.5 molecules/100 eV. This rate, however, is strongly inhibited by CO and thus the rate was assumed to be nearer 1.35 molecules/100 eV in a typical HTGR coolant for Tingey's analysis.

Woodley⁽¹⁵⁰⁾ measured the radiolytic rate of the reaction of water vapor with graphite in the presence of helium and reported a value of 0.75 molecules of carbon removed/100 eV. The products of this reaction are H_2 and CO_2 in contrast with the thermal reaction where CO is the product.

Tingey⁽¹⁵¹⁾ measured the radiolytic rates of the gas phase water-gas shift reaction, $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2$, and reported the rates as a function of temperature from 100 to 500°C. He also used these gas phase reactions to investigate the energy transfer from helium in the range of reactive gas concentrations from a few ppm to 100%. In a recent document Turcotte and Tingey⁽¹⁵²⁾ summarize their results which show that energy absorbed in He is effectively transferred to the reactive species at concentrations down to about 2000 ppm. As the helium purity increases, the radiolytic rate

decreases until at 10 ppm total impurity the rate is approximately 5% of that obtained when the impurity concentration is 2000 ppm or greater. When applied to the Fort Saint Vrain HTGR these results predict only a slight perturbation on the thermal rate of graphite corrosion with a somewhat larger change in the steady-state impurity level.

CARBON-DEPOSITION REACTIONS

The reactions of water vapor, oxygen, and carbon dioxide impurities with the hot graphite of an HTGR core all lead to the production of carbon monoxide in the helium coolant. The carbon monoxide is thermodynamically unstable in the cooler regions of the primary circuit when the gas temperatures drop below 500°C. Under these conditions CO can deposit carbon and regenerate the oxidizing impurities (H₂O and CO₂) which then further corrode the core. This process, generally referred to as the carbon transport cycle, could lead to an accelerated corrosion rate and could also produce carbon dust with its associated problems.

Workers at Gulf General Atomic ⁽¹⁵³⁾ have analyzed the effects of carbon deposition on the HTGR and have identified the following potential problems:

- 1) Carburization of the metal heat exchangers;
- 2) Fouling of heat exchanger surfaces by sooty carbon resulting in poorer heat transfer;
- 3) Adsorption of fission products on the carbon dust with the resultant potential for high fission product release in the event of a primary circuit rupture;
- 4) Production of CO₂ and H₂O which enhance graphite corrosion.

Although the carbon deposition reactions,

tend to proceed in the direction of solid carbon at the coolant temperatures in the heat exchanger, their rates have been shown⁽²⁹⁾ to be low in the absence of a catalytic surface is not well understood, but Palmer and Cullis⁽¹⁵⁴⁾ concluded that metallic iron is catalytic, but iron oxides are not. Some iron carbides are apparently also catalytic while other carbides apparently retard the deposition.

Everett and co-workers in their chapter on Carbon Transport⁽²⁹⁾ have evaluated the potential for carbon transport on the basis of thermodynamics. They point out that carbon deposition occurs only when the following conditions are met: 1) the concentration ratios, $[\text{CO}_2]/[\text{CO}]^2$ in the case of reaction 1 and $[\text{H}_2\text{O}]/[\text{CO}][\text{H}_2]$ for reaction 2 is such that at least one of the reactions is driven in the direction of free carbon and, 2) $\text{H}_2/\text{H}_2\text{O}$ is sufficiently high to maintain iron in the metallic state. For typical impurity concentrations in the HTGR coolant, $\text{H}_2/\text{H}_2\text{O}$ must be less than ten or in the absence of H_2 and H_2O , CO/CO_2 less than one, to insure that deposition of carbon does not occur. Figure 12 illustrates this point graphically, the curve with the positive slope representing $\text{H}_2/\text{H}_2\text{O}$ for the oxidation of iron by steam as a function of temperatures; the other curves show $\text{H}_2/\text{H}_2\text{O}$ for reaction 2 in equilibrium. From these curves, it should be clear that a system containing 10^{-4} atmospheres (about 2 ppm in 50 atm. He) of CO and H_2 will deposit carbon only at temperatures below about 400°C and the process will be catalyzed only when $\text{H}_2/\text{H}_2\text{O}$ exceeds 9. For H_2 and CO concentrations of 10^{-3} atmospheres (20 ppm), the temperature could be as large as 500°C and $\text{H}_2/\text{H}_2\text{O}$ as low as six and still have a favorable condition for catalytic carbon deposition.

Predictions of the steady-state value of $\text{H}_2/\text{H}_2\text{O}$ generally exceed the value of ten but depend on the assumption made. Also the results from Peach Bottom⁽³⁰⁾ indicate that normal H_2O concentrations are immeasurably low. Thus, it currently appears likely that $\text{H}_2/\text{H}_2\text{O}$ will exceed ten and thus carbon deposition is possible.

Carbon deposition apparently can be restricted by using a high chromium alloy because of the stability of Cr_2O_3 . It may also be found with more detailed work that deposition will be retarded with time due to buildup of a carbide film. At present, however, the potential for carbon deposition is not clearly understood and, thus, should be thoroughly evaluated.

GAS DESORPTION FROM GRAPHITE

Graphite and other carbons are well known for their ability to sorb large quantities of gas. This property, though useful to retain released fission products, is the source of substantial quantities of impurities in the coolant stream.

Although several authors⁽²¹²⁻²¹⁵⁾ have investigated the release of gases from graphite, the most pertinent work to HTGR technology is that of Blakely and Overholser.⁽²¹⁵⁾ They measured the desorption of gases from a needle coke graphite which was graphitized to 2800°C and specially fabricated for the Experimental Gas Cooled Reactor (EGCR).

Prior to the measurements, the samples were evacuated to a pressure of 10^{-3} Torr at 30°C to remove any physically sorbed gases. The samples were then heated in steps to 1800°C and the total quantity, as well as the composition of evolved gas, was measured. Table II lists the average data obtained to 1000°C. Heating to 1800°C produced a total volume of evolved gases of 40-50 cm^3 (STP)/100 cm^3 of graphite. The additional evolved gases, after 1000°C, were composed almost entirely of hydrogen and carbon monoxide.

The kinetics of gas desorption was also determined. The volume-time relationships were reported by Overholser to follow an Elovich-type equation of the form, $\text{Volume} = A \log t + B$ where A and B are empirical constants and t is the time.

TABLE II
AVERAGE VOLUME AND COMPOSITION OF
GASES EVOLVED FROM GRAPHITE⁽²¹⁴⁾

Temp.	Gas Volume cm ³ (STP)/100 cm ³ Graphite	Gas Constituents, Vol. %						
		H ₂	Hydro- Carbons	H ₂ O	CO ₂	N ₂	CO	SO ₂
300	0.6 ±0.1	2	8	58	7	17	4	4
600	2.3 ±0.5	7	19	19	20	6	19	10
1000	11.5 ±1.6	37	2	1	2	1	56	1
Total	14.4 2.0	31	5	6	5	2	48	3

IV. IMPROVED NUCLEAR GRAPHITES

In this section we will briefly review a wide range of "improved" nuclear graphites; the designation "improved" has been applied to an extensive range of non-conventionally produced materials^(155,156) (i.e., those where the production technology and/or raw materials⁽¹⁵⁷⁾ differ significantly from those used in the production of electrode graphites). These graphites may be designated as "improved" because of higher strength, reduced dimensional changes, or more isotropic dimensional change behavior, etc. For some applications, one of the "improved" materials may indeed offer significant advantage; for others it may prove to be detrimental in terms of overall design.

Although extensive irradiation testing data have been accumulated on some of these non-electrode types of materials, none have been produced by U. S. manufacturers in the quantities and to the specifications required for reactor construction. Considerable work has been done by manufacturers in other countries to prove capability for producing isotropic graphites in quantities and to the specifications required for power reactor construction;⁽¹⁵⁸⁾ although cost data are not readily available, the production costs appear to be higher than those of electrode graphites, even when produced in quantity.

Molding, especially isostatic molding, can produce a more isotropic body, even from anisotropic cokes, than are produced by extrusion; a wider range of binder/coke mixtures can also be used. Thus, the properties of molded graphites can be tailored over a wider range, for the same starting materials, but costs are generally much higher than for extruded materials and production sizes are more limited.

The use of resin binders and/or impregnants results in increased strength and/or decreased permeability to gases but generally yield a material with decreased dimensional stability.⁽¹⁵⁹⁾

By reducing the calcination temperature of a petroleum coke, progressively less binder material is required to obtain bonding between filler particles; these "raw coke" graphites generally are more isotropic and have higher strengths than conventional nuclear graphites. However, it should be noted that the raw coke graphites have generally been produced by molding and have gained their "improved" designation through comparison with conventional nuclear graphites.^(160,161) Although the situation is not completely resolved, data exist which indicate that the improvement in dimensional stability is a result of molding and that molded calcined-coke based graphites may exhibit as good as or better dimensional behavior than the raw coke materials.

Less ambiguity exists in regard to the behavior of graphites produced from asphalt-based* or gilsonite-based cokes.* The morphology of these materials is quite unlike the morphology of petroleum cokes produced by the delayed coking process. The coke particles are roughly spherical in shape with the crystallites aligned parallel to the adjacent surface; thus, the filler particles are themselves isotropic on a macroscopic scale and tend to impart the same isotropy to the finished body.⁽¹⁶²⁾ Dense, high strength,

*Cokes produced by the destructive heating of a petroleum asphalt or from "gilsonite", a naturally occurring bitumen.

high CTE, isotropic graphites with good dimensional stability have been prepared using these cokes as filler material, and a considerable body of data exists in regard to their irradiation behavior.^(20, 158, 163) Work still needs to be done on the development of a radiation-damage model based on the morphology of these materials.

The same general situation exists in regard to graphites prepared from carbon blacks.^(156,164,165) The carbon black particles are roughly spherical and are isotropic on a macroscopic scale. Carbon blacks produced at low temperatures are generally low density but tend to undergo a large shrinkage during high temperature heat-treatment, and particle densities may then approach 95% of the theoretical graphitic crystallite density. Because of the small particle sizes, generally a much higher percentage of binder is required to produce a structurally sound body than is required for production of coke-based graphites. The resultant carbon black based graphites generally shrink very rapidly at low fluences; however, their isotropy and their subsequent dimensional stability at higher fluences⁽¹⁵⁵⁾ may qualify them for the "improved" designation. Additional work needs to be done on the development of a radiation damage model which is applicable to the full range of particle sizes and morphologies encountered within the general class of materials labeled as carbon blacks.

V. SPECIAL CARBON MATERIALS

Possible HTGR applications for graphite or carbon materials, other than core-quality nuclear grade graphite, include:

- 1) The use of lower-quality nuclear grade (or electrode grade) graphite in the reflector-shield region where life-time fluences are very low;
- 2) The use of graphites or ungraphitized carbons for core support, again where life-time fluences are very low;
- 3) The use of pyrolytic carbon coatings on fuel particles;

- 4) The use of ungraphitized carbon materials as a cement or as a matrix to contain the fuel particles, and
- 5) The use of boron carbide or boronated graphite (i.e., a graphite matrix containing boron in the form of boron carbide) for neutron shielding, control rod material, and/or "burnable neutron poison" to control core reactivity and power distribution.

Because of differences in surface area, effect of impurities, etc., the chemical reactivity of carbons and non-nuclear grade graphites may be quite different than the reactivity of core-grade material; where these materials are exposed to the high temperature gas stream, these differences in chemical reactivity should be considered, irrespective of the radiation environment. In the remainder of this section, however, we shall confine our comments to material applications where significant neutron fluences can be accumulated during the anticipated life-time of the material.

Extensive investigations^(166,168) have been conducted in recent years on the development of coated fuel particles and on the pyrolytic carbon coatings which act as miniature pressure vessels to contain the fission products. Because the technologies involved in the production of fueled particles appears to be well advanced and extensive use has been made of irradiation proof-testing to assure adequate performance of fueled particles under HTGR design conditions, we will not attempt to review this area in any detail.

Bokros⁽¹⁶⁹⁾ has reviewed the deposition, structure and properties of pyrolytic carbons and additional information is available in the recent publications by Kaae.^(170,171) Radiation-induced dimensional changes, mechanical property changes, and creep have been the subject of several recent papers by Bokros and others.⁽¹⁷²⁻¹⁷⁵⁾ Basic data of this type is invaluable for the development of models which can be used to predict performance of coated particles and to analyse the results of irradiation proof-testing programs.⁽¹⁷⁶⁻¹⁷⁹⁾

At the temperatures of interest for HTGR's, low temperature carbons contract at much higher rates than do graphitized materials;^(164,165,180) this is important for materials (such as the low-temperature carbon used to bind fuel particles together) which are used at positions where significant fluences will be accumulated. To counteract the rapid shrinkage of the carbon-binder, a considerable quantity of graphitized filler is included in the fuel compacts. For best performance, the fueled-particle graphitized filler carbon-binder mixture must be adjusted for compatibility with the surrounding graphite. Results of irradiation testing of such composite materials indicate that satisfactory mixtures can be tailored to meet the HTGR fuel compact requirements.⁽¹⁸¹⁻¹⁸⁵⁾

The effects of irradiation on boron carbide has been reviewed by Evans;⁽¹⁸⁶⁾ more recent data have been reported by Stansfield,⁽¹⁸⁷⁻¹⁸⁹⁾ Pitner and others⁽¹⁹⁰⁻¹⁹²⁾ and by Copeland et al.⁽¹⁹³⁾ Although the mechanisms are not completely clear, it is known^(194,195) that the dimensional changes are increased due to atomic displacements caused by the products of the $B^{10}(n,\alpha)Li^7$ reaction and by nucleation of displaced atoms by boron impurities.⁽¹⁹⁶⁾ Although it appears that dimensional changes are not enhanced by conversion of B_4C to B_2O_3 , results by Woodley^(197,198) clearly indicate that B_4C should be protected from water vapor and other oxidants. B_4C is readily oxidized to B_2O_3 and to HBO_2 , which is formed by the reaction $B_2O_3 + H_2O \rightarrow 2HBO_2$. Both the oxide and acid are quite volatile at HTGR temperatures.

VI. SUMMARY AND RECOMMENDATIONS

Graphite and carbons have played a major role in the development of nuclear power production because of their well recognized nuclear properties. With the current interest in the high temperature gas-cooled reactor comes a renewed interest in nuclear graphite. Thus we have attempted to compile a review of the applicable information from many sources on graphite and other carbon materials for HTGR applications.

Although there have been studies to evaluate the nuclear behavior of a wide variety of graphite types, most of the U. S. experience with reactor grade graphites has been limited to extruded materials produced from petroleum coke fillers and coal tar pitch binders. This tendency toward the petroleum coke graphites is primarily due to three reasons:

- 1) A highly developed manufacturing technology for electrode graphite;
- 2) Availability of low cost, large blocks of the material for reactor construction;
- 3) A substantial volume of available data from irradiation testing.

For the same reasons, current U. S. HTGR designs anticipate the use of petroleum coke graphites in spite of potential for the improvement of certain physical and/or nuclear properties by the "improved graphite types". Because of the current demand, this review has treated primarily the behavior of extruded petroleum coke graphites.

Within the range of temperatures of interest (400-1200°C) and the fluences anticipated for HTGR designs, these petroleum coke graphites initially shrink in all dimensions and continue to contract in the direction parallel to their axis of extrusion, but may "turnaround" and begin to expand in the two directions orthogonal to the axis of extrusion before reaching design fluences. Various important parameters for nuclear applications such as contraction rates, the fluence at which turnaround occurs, percent contraction at turnaround, and expansion rates after turnaround are strongly dependent on graphite morphology and on irradiation temperature and imposed stresses.

The data included in this review are intended to be representative of those necessary to evaluate the design of an HTGR. We have also attempted to give an indication of the variability of the data to enable the reader to determine the limits of possible behavior of the graphites. It has become increasingly clear to the authors that the properties of graphites are as varied as the forms of graphite. Carbon is well recognized as a highly versatile material because of the degree to which its properties can be varied through the selection of raw materials and variation of manufacturing parameters; but, in turn, care must be taken to assure that those parameters are well understood and controlled to obtain the desired properties.

Areas of particular significance are the effects of temperature, flux intensity, internal and externally applied stresses, and graphite size on the irradiation behavior of the graphite components. Most of these effects are reasonably well understood at low fluence, but at the higher fluences projected for some components near the end of their design-life, further understanding is desired. Prediction of changes at high fluences currently cannot be made with certainty because of the possible interactions between the various phenomena.

The chemical behavior of carbon is also highly dependent upon the morphology of the carbon of interest. Rates of reaction may change over several order of magnitude depending upon catalytic impurity levels and upon structure. Thus care should be taken to evaluate these effects in predicting rates for the specific graphite of interest. Radiolytic effects on the reactions of impurity gases appear to be relatively small for HTGR's, but they should be thoroughly evaluated in determining the chemistry of the coolant system.

The potential for carbon deposition from CO disproportionation is an area where special consideration should be given to insure that detrimental or potentially undesirable interaction will not occur.

Some of the specific areas where additional information may be required in order to accurately project the effects of phenomena which may have a direct bearing on economic reactor operation and projected component life include:

- 1) Where radiation-induced creep rates can have a significant effect on dimensional changes, the effect of creep strain at high fluences and the possibility that the creep rate "constants" may not remain constant at high fluences needs additional investigation;
- 2) Analysis of existing data could provide a much firmer basis, than is possible at the present time for projecting irradiation data from one reactor facility to another position where differences exist in neutron spectra and flux intensities;
- 3) Where the predicted behavior of reactor components is based on data obtained from pre-production lots of graphite, sufficient data should also be compiled on the production lots of material to allow correlations to be made over the full range of projected operating conditions;
- 4) Where projected behavior, especially at high fluences, is based on combination of several effects, fairly sophisticated computer models may be required to accurately predict the changes; additional work needs to be done to determine the degree of uncertainty to be expected and to identify areas where improvements in the computer models are needed;
- 5) Because of the accumulated uncertainties in projections which are dependent on the interaction of several different phenomena, it is highly recommended that a comprehensive program be undertaken to monitor the changes in dimensions, chemical behavior, and physical properties of graphite for each new HTGR design.

FIGURE 1: Normal Sampling Scheme for Rectangular Extrusion.

FIGURE 2: Normal Sampling Scheme for Cylindrical Extrusions.

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FIGURE 3: Typical Radiation-Induced Length Changes--NC8 ($\perp$) Samples.

FIGURE 4: Typical Radiation-Induced Length Change - NC8 (||) Samples.

FIGURE 5: Radiation-Induced Volume Changes - NC8 Graphite.

FIGURE 6: Comparison of Radiation-Induced Length Changes at $900 \pm 50^\circ\text{C}$.

FIGURE 7: Comparison of Radiation-Induced Length Changes at $1175 \pm 25^\circ\text{C}$.

FIGURE 8: Typical Radiation-Induced Length Changes - H327A($\perp$) Samples

FIGURE 9: Typical Radiation-Induced Length Changes - H327A (||) Samples.

VARIATION OF CREEP RATE WITH IRRADIATION TEMPERATURE

FIGURE 10: Variation of Creep Rate With Irradiation Temperature.

FIGURE 11: Thermal Expansion of H327A Samples.

FIGURE 12: Equilibrium Conditions Required For The Formation Of Solid Carbon From The Reaction $\text{CO} + \text{H}_2 \rightleftharpoons \text{C}_{(s)} + \text{H}_2\text{O}$.

APPENDIX ANEUTRON DOSIMETRY AND DAMAGE ANALYSIS

de Halas⁽¹⁹⁹⁾ and Reynolds⁽²³⁾ have reviewed the basic aspects of neutron fluence and atomic displacement rates for the correlation of graphite irradiation data. Therefore, in this section we shall confine our discussion to the practical aspects of using data obtained in one reactor facility to predict graphite behavior at some position in another reactor.

Radiation-induced changes in dimensions and physical properties are the result of two competing processes which occur simultaneously during an irradiation; these are: 1) The rupture of carbon-carbon bonds and displacement of an atom from a fixed position in the graphite aggregate and 2) The establishment of new bonds as the atom comes to rest at a new position. It should be realized that the new rest position may be either identical to or very different from the position from which the atom was displaced and, moreover, the displaced atom may leave behind a vacancy (a hole in the graphite lattice) which may remain, may agglomerate with other vacancies, or may disappear at a crystal edge, etc.

The "damage rate" then, is a complex function of the atomic displacement rate (which depends on neutron flux intensity and the neutron energy spectrum), the migration rates of displaced atoms, vacancies and complex agglomerations of these defects (which are primarily dependent on irradiation temperature), and the current number and distribution of all other defects (which depends on prior history of the sample).

Even at one position in a reactor, the neutron flux intensity and/or neutron energy spectrum can change with power level, with changes in isotopic content of adjacent fuel, with changes in composition of materials surrounding that point, etc. Furthermore, even larger differences can be encountered in moving from one position to another within the same reactor. Irradiation time is, therefore, not a sufficient quantity for the correlation of irradiation effects.

A more useful quantity is the neutron fluence (i.e., the neutron flux intensity multiplied by the irradiation time). By measuring the activity of neutron monitors which have been irradiated with the samples, one can calculate the neutron flux intensities at the various irradiation positions and express the accumulated fluences as, say, "equivalent fission fluences". For all convenient monitors, however, the efficiency of neutrons with different energies to activate the monitor is quite different from their efficiencies to produce displacements in graphite. Thus, the ratio of the displacement rate to activation rate will vary between reactor facilities and, in general, will be different for different neutron spectra.

Four general procedures can be used to correlate irradiation data obtained in different irradiation facilities, these are:

- 1) For graphite moderated reactors only, one can establish an empirical function for damage rate (i.e., the rate of change of one or more properties) as a function of radial distance from a reactor fuel tube and the power generation rate in the fuel; one can then calculate the damage rate at any position in a similar reactor by summing the contributions from all fuel tubes adjacent to the position of interest;⁽²⁴⁾
- 2) One can establish an empirical correlation factor from the ratio of the rates-of-change of a property per unit fluence at equivalent temperatures in two different facilities;⁽²⁴⁾
- 3) One can calculate the relative number of displaced atoms per unit fluence by the use of theoretical displacement cross sections and calculated neutron spectra,⁽²⁰⁰⁻²⁰¹⁾ or
- 4) One can use measured neutron spectra and the differences in damage rates in several reactor facilities, which have very different neutron spectra, to derive an empirical damage cross section as a function of neutron energy.⁽²⁰²⁾

The first method has been applied to some extent in both the U.K. and the U. S.; the second and third methods are, however, more general and are more widely used. Although the fourth method has been used extensively for correlation of irradiation data on metals, it has not yet been applied to graphite irradiation data.

A variation of the third method, which was first proposed by Dahl and Yoshikawa,⁽²⁰³⁾ has become widely used, especially by U. S. investigators. Dahl and Yoshikawa showed that the calculated number of atomic-displacements per unit fluence is practically independent of the neutron energy spectrum if the fluence is measured in units of neutrons with energies greater than 0.065 MeV; moreover, this independence was maintained even when quite different models were used for the theoretical displacement cross sections. This result has been recently reconfirmed by other investigators.⁽²⁰⁴⁻²⁰⁶⁾ Because of convenience, however, it has become more customary to express fluences in terms of neutrons with energies greater than 0.18 MeV ($E > 0.18$ MeV) rather than greater than 0.065 MeV; Dahl⁽²⁰¹⁾ has shown that the ratio of calculated atomic displacements per unit fluence ($E > 0.18$ MeV) varies less than $\pm 10\%$ over a wide range of neutron spectra. Reed et al.⁽²⁰⁷⁾ recently reconfirmed Dahl's results using a different model for the theoretical displacement cross sections and calculated neutron spectra for a wide variety of graphite moderated reactors.

The subject of neutron fluence and atomic displacement rates in U. S. graphite irradiation facilities has recently been reviewed by Morgan.⁽²⁰⁸⁾ Gray and Thorne⁽²⁰⁹⁾ have reviewed the intercalibration of graphite irradiation facilities used by U.K. investigators and Genthon⁽²⁰⁵⁾ has reviewed the intercalibration program in France. Valette⁽²⁰⁶⁾ and Reed⁽²⁰⁷⁾ have reviewed the intercalibration programs for the DRAGON and THTR Projects as well as extension of calculational methods to other designs of HTGR power reactors. Zijp and Rieffe⁽²¹⁰⁾ have compiled intercalibration factors obtained both from calculations and from empirical comparisons of property change data.

Four principle units of fluence have been used for reporting graphite irradiation data of interest to HTGR designs:

- 1) $E > 0.18$ MeV: The fluence of neutrons with energies greater than 0.18 MeV has been used for reporting data from the USAEC nuclear graphite program at Battelle-Northwest, the Gulf General Atomic's irradiation program and recent data from the THTR program in Germany;

- 2) $E > 0.05$ MeV or $E > 50$ KeV: The fluence of neutrons with energies greater than 50 KeV has been used to report data from ORNL graphite irradiations in HFIR:
- 3) DIDO equivalent fission flux, DIDO nickel dose, or DIDO eq (Ni):
The equivalent fission fluence measured by the $\text{Ni}^{58} (n,p) \text{Co}^{58}$ activation reaction in an empty channel of DIDO which would produce the same calculated number of displacements as calculated for the irradiated sample has been adopted for reporting most of the data from UK, EURATOM, and OECD investigators;
- 4) $\phi_R(G)$: The equivalent fluence, calculated in terms of the fraction of the fission spectrum above 1 MeV, which would produce the same calculated number of displacements as calculated for the irradiated sample is currently being used by French investigators.

It has recently been recommended* that all future graphite irradiation data be reported in terms of an internationally consistent fluence scale, "equivalent fission fluence for damage in graphite" (ϕ_G), which is defined by:

$$\phi_G = \frac{\int_{t_1}^{t_2} \int_0^\infty \sigma_s(E) p(E) \phi(E,t) dE dt}{\int_0^\infty \sigma_s(E) p(E) \chi(E) dE / \int_0^\infty \chi(E) dE}$$

Where $\phi(E,t)$ is the absolute flux density spectrum at time t

$\sigma_s(E)$ is the scattering cross section of carbon

$p(E)$ is the atomic displacement weighting function, and

$\chi(E)$ is the fission spectrum.

*Recommended by the delegates (representing the I.A.E.A., EURATOM, U.S.A.E.C. and individual laboratories from six countries) attending the "Specialist's Meeting on Radiation Damage in Graphite", which was held on October 30, 1972, at the Battelle Seattle Research Center under the cosponsorship of the International Atomic Energy Agency and Battelle Memorial Institute.

The Thompson and Wright model,⁽²¹¹⁾ which has been widely used for the intercomparison of graphite irradiation facilities, is being used at present for $p(E)$ for fission reactor irradiations, but provision has been made to standardize on a more realistic physical model when one has been demonstrated to give acceptable agreement with experimental data.

Table III shows the best estimate for conversion of the other principle fluence scales to equivalent fission fluence for damage in graphite (ϕ_G).

TABLE III
CONVERSION OF FLUENCE SCALES

<u>To Convert From Fluence Reported In Terms Of:</u>	<u>To Equivalent Fission Fluence, ϕ_G, Multiply By:</u>
(E > 0.18 MeV)	1.18
(E > 0.05 MeV)	0.89
DIDO eq. (Ni)	1.77
$\phi_R(G)$	0.97

In the U.K. where it has been necessary to correlate irradiation data from reactors in which the neutron flux intensities might vary by more than an order of magnitude, it has been found necessary to correct the irradiation temperatures for the effect of flux intensity or, more properly, the differences in atomic-displacement rates. Although there has been some disagreement as to the magnitude of the correction and, especially for higher temperatures, even the necessity for making a temperature correction, it is generally accepted that irradiation data obtained at measured absolute temperature θ_i , in a reactor facility where the atomic displacement rate is D_i , must be assigned an equivalent absolute temperature θ_e , calculated from the equation:

$$\frac{1}{\theta_e} = \frac{1}{\theta_i} + \frac{K}{Q} \ln \frac{D_i}{D_e}$$

if applied to another reactor having a displacement rate D_e ; where K is the Boltzman constant and Q , the activation energy for defect annealing, is equal to 1.2 eV.

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