STP-NU-009

# GRAPHITE FOR HIGH TEMPERATURE GAS-COOLED NUCLEAR REACTORS



ASME STANDARDS TECHNOLOGY, LLC

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# GRAPHITE FOR HIGH TEMPERATURE GAS-COOLED NUCLEAR REACTORS



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Date of Issuance: September 3, 2008

This report was prepared as an account of work sponsored by ASME Pressure Technology Codes & Standards and the ASME Standards Technology, LLC (ASME ST-LLC).







ASME Standards Technology, LLC
Three Park Avenue, New York, NY 10016-5990

ISBN No. 0-7918-3176-0

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## FOREWORD

This report is intended as an introduction to the burgeoning field of graphite high temperature gas-cooled nuclear reactors with particular emphasis on nuclear graphite.

There is a brief review of the use of bulk graphite as a moderator in fission reactors around the world from the beginnings in 1942 to Generation IV prismatic and pebble bed High Temperature Reactor (HTR) potential. The characteristics, manufacture, properties and irradiation behavior of bulk graphites are outlined. A bibliography is provided for further study.

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## ABSTRACT

This technical report presents the basic information relative bulk graphite production, structure, chemical properties, physical properties and neutron irradiation behavior. Bulk graphite characteristics, its manufacture, properties and irradiation behavior as well as a new generation of nuclear grades are briefly reviewed. An overview of graphite moderated gas-cooled reactor designs is also presented. The report serves as a summary of the training seminar on Nuclear Graphite conducted during the ASME Boiler and Pressure Vessel Code week, October 30–November 3, 2006, in Louisville, KY.

There is no universally accepted code for the design of graphite moderator structures. The history of graphite moderated reactors is traced from the beginnings in 1942 to the most recent utility start-up in 1989. Developments have continued over the intervening years especially in the area of helium cooled High Temperature Reactors. Prismatic 30MWth, and pebble-bed 10MWth, test reactors were brought into operation in Japan and China, respectively.

# 1 INTRODUCTION

Graphite has extraordinary abilities to both slow down fast neutrons and to sustain the collateral damage. In particular, structural integrity is retained over a wide range of neutron fluence and reactor temperatures such that commercial graphite moderator systems have run for over forty years.

Graphite is a member of a class of materials known as moderators which are effective in slowing high energy fission neutrons to thermal energies so as to maximize fission collisions. (Other moderators include beryllium, beryllium oxide, heavy water and water as well as certain metal hydrides and certain hydrocarbons.) The slowing down of neutrons is the result of multiple collisions with the nuclei of the moderator.

Graphite produced synthetically in large blocks is particularly attractive as a moderator because it is produced in quantity around the world by relatively simple industrial processes in a wide range of sizes and grades at reasonable cost. (In this report, blocks of synthetic graphite will be termed bulk graphite as distinct from other forms such as single crystal, powder and fibers.) The blocks are readily machined into quite intricate shapes. Furthermore, graphite is refractory in the sense that, in the absence of both air and neutron irradiation, at temperatures up to about 2000˚C, structural integrity is retained. The strength is actually enhanced: for instance, the tensile strength of graphite at 2000˚C is about 50% higher than its room temperature value.

Thus, it should come as no surprise that the first fission reactors in the USA (1942), the USSR (1947), the UK (1947), Belgium (1956) and France (1956) were all graphite moderated. The early civil power reactors in France, the UK and the USSR were large-scale derivatives and currently form the backbone of nuclear electricity generation in the UK.

The refractory capability of graphite moderated reactors is evident in the increase in coolant gas outlet temperatures from 140˚C in the early air-cooled versions to 950˚C in the helium cooled pilot units in Germany and Japan. There is great interest around the world in the commercial exploitation of the high helium gas temperatures for the production of hydrogen, sea water desalination and direct cycle power generation.

Currently, there is no universally accepted code for the design of graphite moderator structures. In 1990, ASME (Section III, Div. 2) issued a draft code proposal for Graphite Reactor Core Supports. More recently, a diverse group of Generation-IV Very High Temperature Reactor (VHTR) stakeholders have expressed the need for a unified approach to design code. The stakeholders include the DOE and the NRC in the USA, the nuclear regulator in the Republic of South Africa and the designers AREVA, General Atomics and the PBMR Company. Therefore, an ASME Project Team on Graphite Core Components was established in 2002, initially under Section II. The Team was re-assigned to Section III in 2006. The work of the Project Team had matured and justified the preparation of a training seminar on Nuclear Graphite for presentation during the Louisville ASME Code week, Oct. 30–Nov. 3, 2006. The seminar focused on bulk graphite production, structure, chemical and physical properties and neutron irradiation behavior.

The aim of this technical report is to capture the essentials covered in the Louisville seminar and to provide a brief introduction to nuclear graphite.

# 2 DEFINITIONS

(See also ASTM C 709 on Terminology Relating to Manufactured Carbon and Graphite)

***Anisotropy*** – defined in terms of properties:

> ***With grain*** – parallel to extrusion direction, perpendicular to molding axis.
>
> ***Against grain*** – perpendicular to extrusion axis, parallel to molding axis.

***Crystallite*** – fundamental region of three dimensional order as revealed by X-ray diffraction.

***Grain*** – filler particle (calcined coke, recycled graphite).

***Isotropy Ratio*** – usually defined in terms of the ratio of the thermal expansion coefficient (measured over a defined temperature range) (against-grain)/(with-grain).

***Isotropic Graphite*** – a graphite in which the ratio of the against-grain to with-grain value of the coefficient of thermal expansion measured from 25˚C to 500˚C is between 1.0 and 1.1.

***Near-Isotropic Graphite*** – a graphite in which the ratio of the against-grain to with-grain value of the coefficient of thermal expansion measured from 25˚C to 500˚C is between 1.1 and 1.15.

***Nuclear Graphite*** – any bulk graphite with the desired properties, suitable and known irradiation behavior, with unwanted impurities removed. (See also ASTM D7219 Standard Specification for Isotropic and Near-Isotropic Nuclear Graphites.)

***RMBK*** – reaktor bolshoy moshchnosti kanalniy (Russian)

# 3 GRAPHITE MODERATED GAS-COOLED REACTORS

## 3.1 Developments 1942–1989

The early graphite moderated reactors in the USA, the USSR, the UK and France were dedicated to the production of plutonium, the fundamental investigations of fission and graphite behavior and the preparation of radioisotopes. The operating temperatures were initially relatively low (typically <150˚C) and cooling was achieved indirectly with air initially and more commonly with water. The Hanford reactor cores were contained in a mixed gas blanket of helium and carbon dioxide. However, the potential for harnessing the heat released to raise steam for turbine generation of electricity was recognized.

The first generation of graphite moderated civilian power reactors in France and the UK were cooled directly with carbon dioxide. In the reactors of the former Soviet Union, heat was removed from the RBMK 1000MWe cores indirectly by cooling water. The RBMK graphite core was contained in a mixed gas blanket of helium and nitrogen, typically a 90%/10% mixture.

The first electric utility systems in the UK (so-called Magnox because of the alloy used to contain the fuel) were relatively small (49MWe per reactor, Calder Hall 1957), growing to 490MWe per reactor in the final build (Wylfa 1972, scheduled to close in 2010). A complication with these commercial Magnox reactors was the concomitant radiolytic oxidation. Some mitigation was achieved with small amounts of hydrogen and methane in the coolant circuit. The same grade of medium grain, high purity, extruded needle coke graphite, grade PGA, was used in every Magnox reactor.

A second generation of graphite moderated electric utility reactors were built in the UK between 1976 and 1989 with a combined generating capacity of almost 9GWe. These so-called Advanced Gas-cooled Reactors (AGR) were all relatively large at 555MWe to 625MWe per reactor. Each reactor required about 3000 tonnes of graphite. The graphite grade, GCMB (also known as Gilsocarbon), was a medium grain molded isotropic type using coke produced from Gilsonite, a natural asphalt occurring in Colorado and Utah. A typical arrangement of the graphite moderator blocks in an AGR core is shown in Figure 1. The last AGR station is scheduled to be closed in 2022, representing an average generating life of about 35 years.

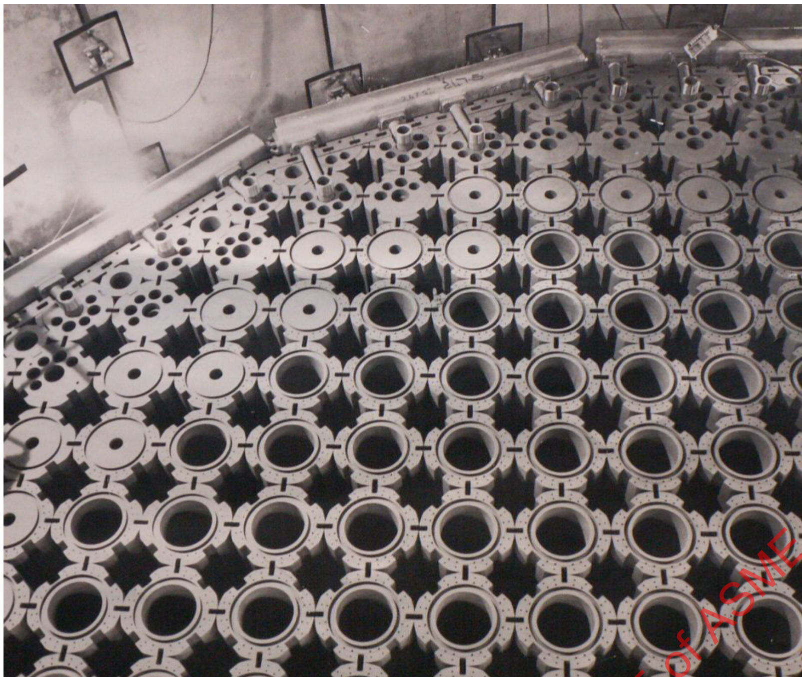


**Figure 1 - The Arrangement of Graphite Moderator Blocks in an Advanced Gas-Cooled Reactor Core [10]**



The gas coolant in the AGR is carbon dioxide. Therefore, radiolytic oxidation of graphite is a life-limiting factor. Significant mitigation of oxidation effects is achieved by small amounts of carbon monoxide and methane in the coolant. A logical development is the deployment of helium as the coolant with the potential of higher gas outlet temperatures. Development work on helium cooled High Temperature Reactors (HTR) was carried out in the 1960s and 1970s in the USA (Peach Bottom), UK (OECD Dragon Project) and Germany (Julich AVR). The latter was a novel departure from the large fixed prismatic beds of graphite blocks and involved the slow movement of both graphite moderator pebbles and fuel pebbles (the pebbles are essentially spheroidal and about the size of tennis balls) through a large cylindrical pressure vessel lined with graphite. A commercial derivative of 300MWe was built in Germany and was operated 1985–1989. Development of HTR in the USA culminated in the Fort St. Vrain 330MWe station which ran for 10 years until premature closure in 1989 caused by chronic water seal leaks.

## 3.2 Next Generation High Temperature Reactors

The renewed interest in nuclear power is fueled in part by global warming and the drive to energy systems which do not generate carbon dioxide. There is special interest in graphite-moderated helium-cooled systems because of the high temperature of the helium exit stream. Where the AGR cores were limited to gas outlet temperatures of ~650˚C, current HTR technology is capable of 850˚C. There is interest in pushing the exit temperatures to 1000˚C in the so-called Very High Temperature Reactor, VHTR. (The term HTR in this report covers both eventualities.) The hot helium can be fed directly to turbines for electricity generation (this direct Brayton cycle is 48% efficient compared with 34% for the traditional nuclear and fossil fuel systems involving intermediate heat exchangers and steam fed turbines). Alternatively, hot helium can be used for process heat in desalination or hydrogen production.

As mentioned earlier, there are two principal configurations of graphite in the new generation of High Temperature Reactors.

### 3.2.1 Prismatic

The commercial prismatic design was pioneered by General Atomics (GA) of San Diego in the 1960s. The graphite is arranged in rows and columns of hexagonal blocks, typically ~14 in. across the flats and 32 in. long. The fuel is loaded in a concentric ring of fuel element blocks, which are removed when the fuel is depleted. Refueling involves new blocks, so the graphite subject to the most extreme irradiation is periodically replaced, allowing the potential for a core life of 60 years. Two multi-holed fuel element blocks are shown in Figure 2. Typical elevation and plan views are shown in Figure 3 and Figure 4.


**Figure 2 - GT-MHR (HTR) Graphite Fuel Element Blocks**
(Courtesy of R. Bratton, INL.)

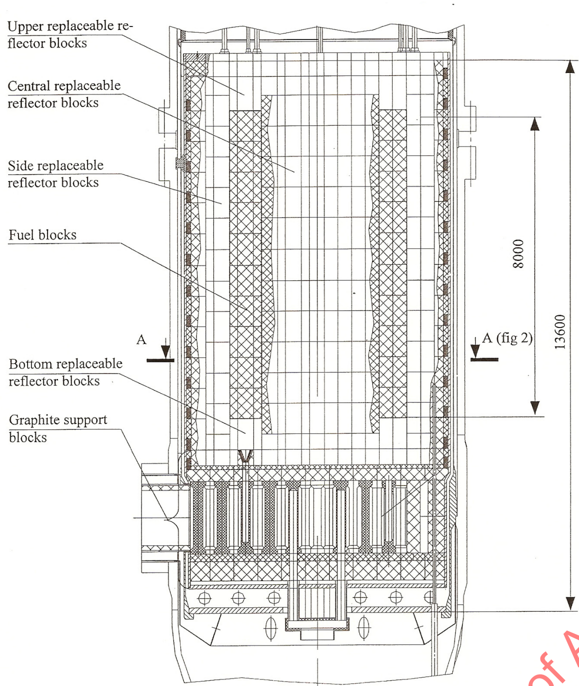



**Figure 3 - GT-MHR (HTR) Prismatic Core: Elevation View (USA, USSR, Japan, France)**

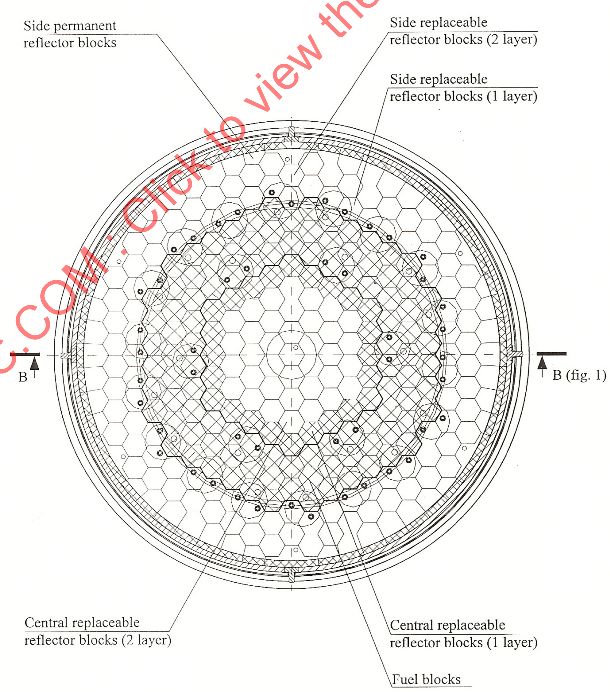



**Figure 4 - GT-MHR (HTR) Prismatic Core: Plan View**

The largest prismatic HTR power reactor (330MWe) ran at Fort St. Vrain, Colorado from 1979 to 1989. In the 1970s, GA offered the GT-MHR (Gas Turbine – Modular High temperature Reactor) in modules of 286MWe. The design was updated in the 1990s for burning Russian weapons grade Plutonium. Prismatic designs by GA and Areva have been proposed for the DOE hydrogen initiative at the Idaho National Laboratory (INL), Idaho Falls, Idaho.

A 30MWth prismatic research reactor brought on line in 1998 is in operation at the JAEA facility, Ibaraki, Japan.

### 3.2.2 Pebble Bed

The pebble bed system was selected by the South African utility ESKOM for exploitation as a Pebble Bed Modular Reactor (PBMR). This new generation of Pebble Bed Reactor, a derivative of the German design, includes a central column of graphite blocks. The fuel and moderator pebbles pass slowly through the vertical annulus between the central column and the outer cylindrical wall of graphite blocks. Schematics are shown in Figure 5 and Figure 6. A small section of the outer graphite wall is shown in Figure 7. Plans call for the building of a 165MWe module at Koeburg in the Republic of South Africa. A PBMR has been proposed for the DOE hydrogen initiative at INL.

A 10MWth research reactor (HTR-10) has been in operation in China since 1998.

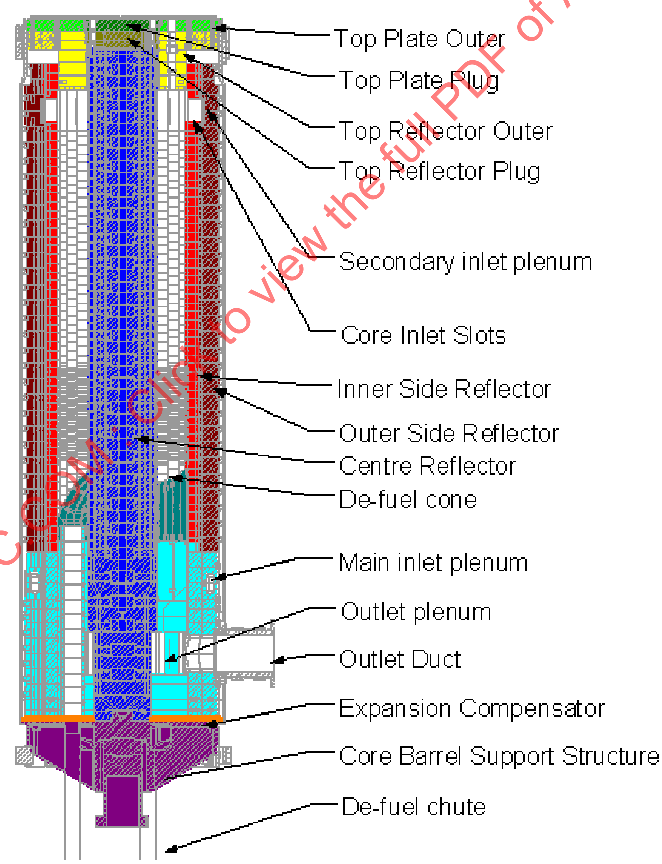



**Figure 5 - General Arrangement of the PBMR Core Structure [11]**

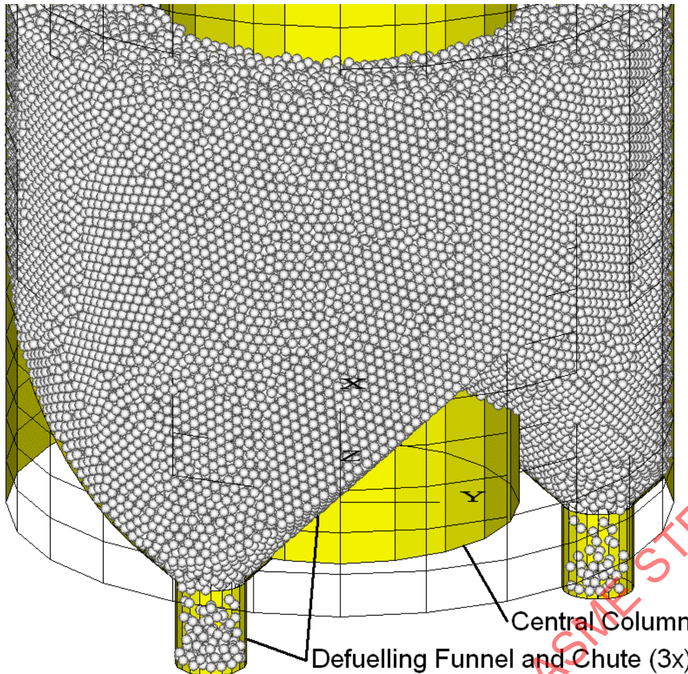



**Figure 6 - PBMR Fuel and Moderator Pebbles - Schematic [12]**

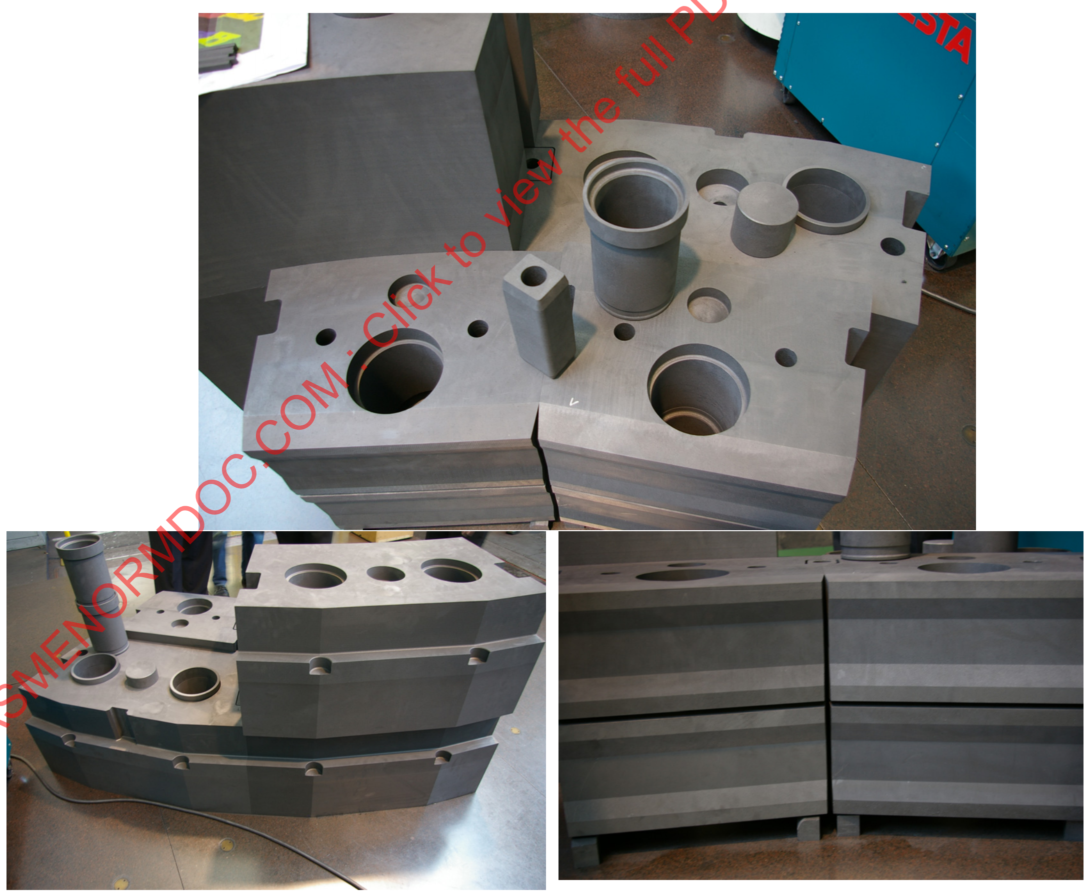


**Figure 7 - PBMR Graphite Outer Wall Components [13]**

# 4 GRAPHITE

Notable characteristics of bulk graphite are summarized in Table 1. Graphite is very different from the kinds of alloy steels used in light and heavy water nuclear reactor pressure vessels. Where an alloy steel has high strength, ductility, no porosity and homogeneity, bulk graphite has low strength and is brittle, porous and inhomogeneous. Some of the differences are quantified in Table 2.

**Table 1 - Notable Characteristics of Graphite**

| |
|---|
| Wide variation in measurable properties with no change in chemical composition |
| No phase changes |
| Chemically inert (with some exceptions) |
| Strength improves at temperatures up to 2000˚C (provided oxidizing gases are excluded) |
| High resistance to thermal shock |
| Ability to slow down (moderate) fast neutrons |



**Table 2 - Graphite and Steel Alloy Property Comparison**

| Property | Steel Alloy 316L | Specialty Extruded Graphite |
|---|---|---|
| Density, #/cu.ft; g/cc | 500, 8.0 (Porosity=0%) | 108; 1.74 (Porosity=23%) |
| Tensile, psi | >70,000 | 2150/1600 wg/ag |
| Elongation at break, % | >40 | 0.3 |
| Poisson's ratio | 0.3 | 0.2 |
| YM, Mpsi | 28 | 1.6/1.2 wg/ag |
| Specific heat, btu/#F | 0.12 | 0.24 |
| Thermal conductivity, W/mK | 17 | 160/145 wg/ag |
| Coefficient of thermal expansion, CTE, (RT-100C) ppm/C | 18 | 2.5/3.6 wg/ag |

A distinctive characteristic of graphite is its anisotropy. This anisotropy is reflected in Table 2 where the notations wg (with grain) and ag (against grain) are introduced. The anisotropy originates in the fundamental crystal structure of graphite (see Figure 8) and is manipulated through raw material (calcined coke) selection, particle sizing and forming method. Further evidence of extreme anisotropy of single crystal graphite is shown in the properties summarized in Table 3. The carbon atoms in industrial bulk graphite can be regarded as assemblies of crystallites (entities which are appreciably smaller than single crystals) which may show some net orientation as in with grain. Other orthogonal references in common use include parallel to the direction of extrusion, or molding, and perpendicular to the direction of extrusion, or molding.

- Layered structure
- In plane: hexagonal net of 3-fold coordinated sp2-hybridised C atoms (graphene sheet). Bond length 143 pm
- Interlayer bonding – van der Waals (= intermolecular) weak bonds, 20-40 MeV/atom
- Planes easily glide and cleave
- ABAB… stacking is most common (ABCABC… is possible)
- Parallel to graphene sheet is the a-axis; perpendicular is the c-axis
- Crystallite height is Lc and diameter is La

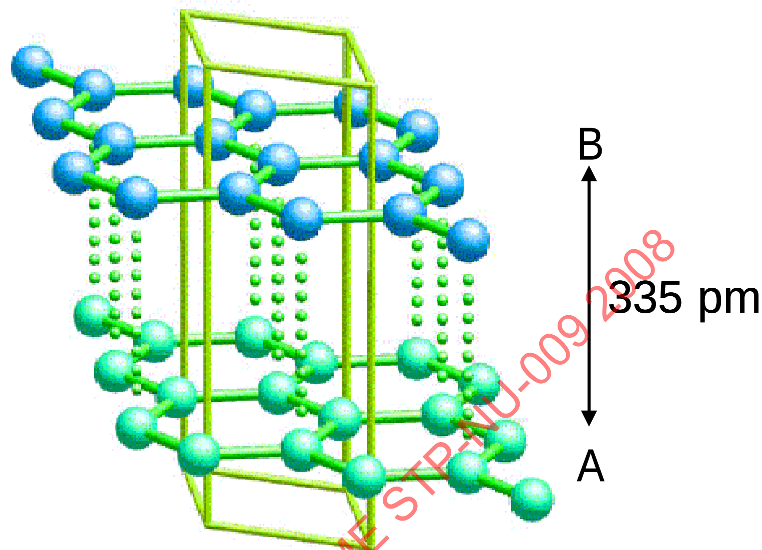



**Figure 8 - Graphite Crystal Structure**
(Courtesy T. D. Burchell, ORNL)



The typical properties of a wide range of commercial graphites in Table 4 can be seen to be a fraction of the values for single crystal in Table 3.

**Table 3 - Room Temperature Properties of Single Crystal Graphite, Density 2.25g/Cc**

| Property | In-the-Basal Plane, a-axis | Across-the-Basal Plane, c-axis |
|---|---|---|
| Tensile, Mpsi (estimated) | 13.9 | 4.9 |
| YM, Mpsi | 148 | 5.3 |
| Thermal conductivity, W/mK | ~2000 | 10 |
| Coefficient of thermal expansion, CTE, (RT-100˚C), ppm/C | -0.5 | 27 |
| Specific electrical resistivity, micro.ohm.m | 0.40 | ~60 |

**Table 4 - Typical Properties of Bulk Graphite**
(data from GrafTech Holdings Inc, website)

| Property | Extruded Electrode, AGX | Extruded Specialty, CS | Molded Specialty, PGX | Isomolded Specialty, ATJ |
|---|---|---|---|---|
| Max grain size, mm | 12 | 0.8 | 0.8 | 75 microns |
| Bulk density, g/cc | 1.70 | 1.74 | 1.73 | 1.76 |
| Flexural strength, psi, wg/ag | 1320/1015 | 3050/2250 | 1600/1300 | 4500/4040 |
| YM, Mpsi, wg/ag | 1.1/0.7 | 1.6/1.2 | 1.0/0.7 | 1.4/1.4 |
| Thermal conductivity, W/mk, wg/ag | 168/101 | 160/145 | 125/104 | 125/110 |
| Specific electrical resistance, micro.ohm.m, wg/ag | 5.5/- | 7.1/9.4 | 10.1/13.8 | 10.5/11.7 |
| Coefficient of Thermal Expansion, (RT-100˚C),l ppm/C, wg/ag | 0.4/1.1 | 2.5/3.6 | 2.2/2.6 | 2.2/2.8 |
| Ash, ppm | 5000 | 800 | 700 | 900 |

## 4.1 Manufacture

At its simplest, bulk graphite is produced from sized carbonaceous fillers held together with a carbon-rich binder, formed into a desired shape, then heat treated first at ~1000˚C and then again at ~3000˚C. In reality, the required calcined cokes (previously subjected to ~1300˚C) are produced from selected petroleum distillates and residues, coal tar or natural asphalts such as Gilsonite (see Figure 9). Calcined cokes vary significantly in shape (see Figure 10) depending upon both the quality of the feed to the delayed coker and the coking conditions. The shape spectrum is defined by needle at one end (the preferred coke for electric furnace steel making, resulting in grades like AGX in Table 4), and isotropic at the other end (the grade CS in Table 4 is produced from coke somewhere along the shape continuum).

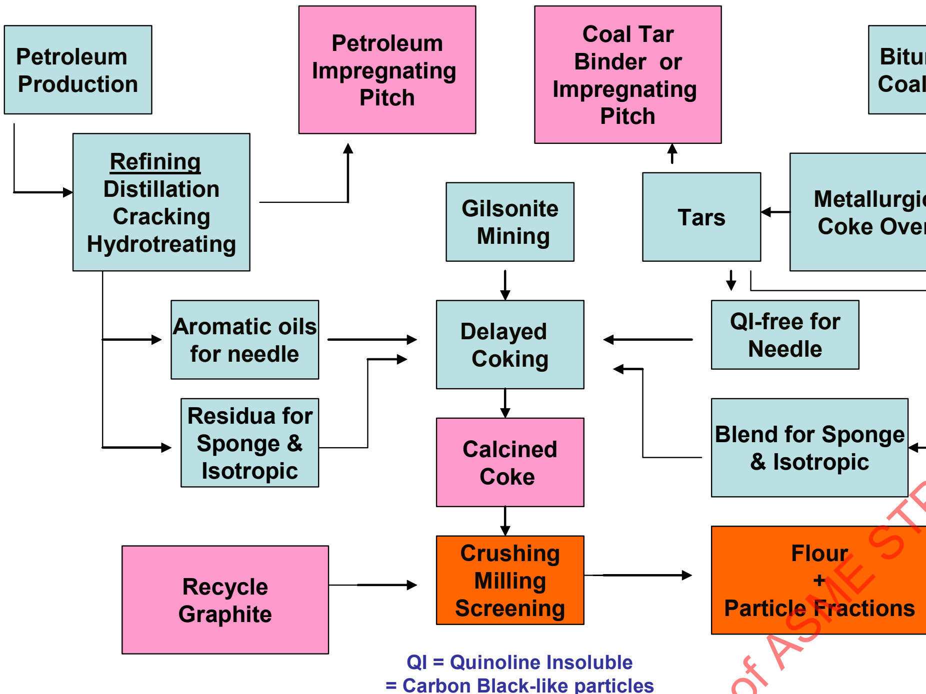
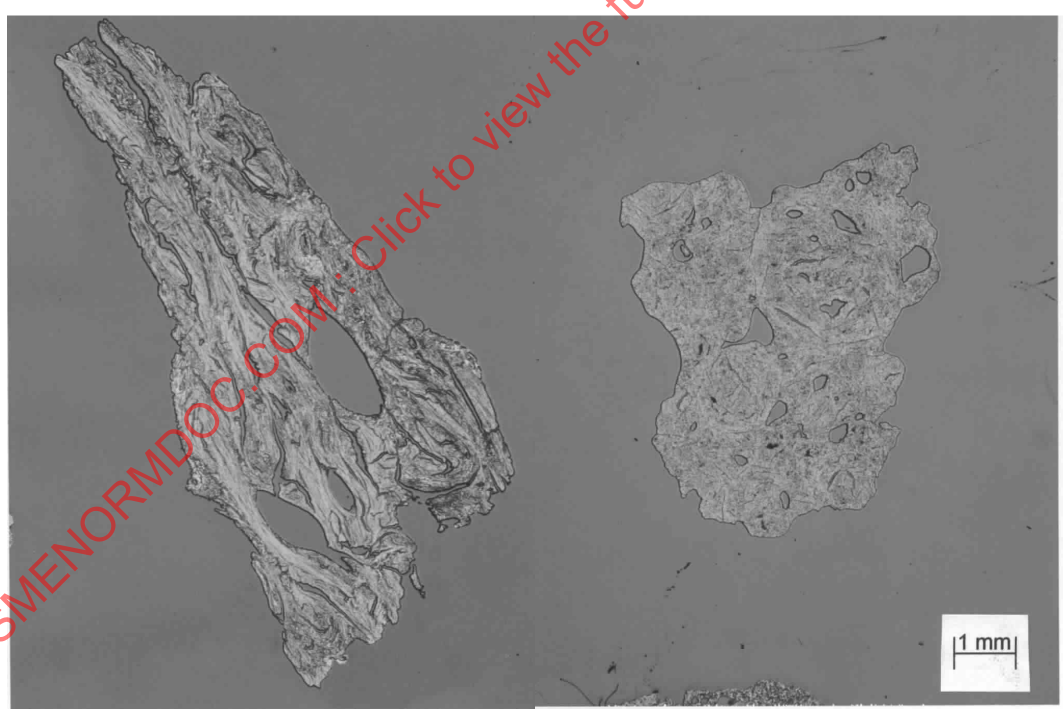



**Figure 9 - Raw Material Sources for Bulk Graphite**




Needle Isotropic

**Figure 10 - The Shape of Calcined Coke Particles [14]**

The binder is typically derived from coal tar, has a softening point of ~110˚C (ASTM D 3104) and a significant yield of carbon on carbonization.

The steps involved in graphite making are (see also Figure 11):

(1) Calcined coke is ground and sized into the required sizes and a portion is milled into a fine flour.

(2) The required calcined coke fractions are hot mixed with coal tar binder pitch.

(3) The hot mix is formed (see Figure 12) into the desired shape. Typically, coarse and medium grain grades (see Table 5 for definitions) are ram extruded, uniaxially molded or vibration molded. The latter is a process unique to SGL Carbon and involves vibrating the mold containing the hot mix while a mechanical pressure is applied parallel to the major axis. Fine grain mixes may be ram or screw extruded or isomolded. The ultrafine and microfine grades are usually isomolded. (A slightly different sequence is used for isomolded grades. The hot mix is cooled, milled into a molding powder, loaded into a rubber bag and pressed isostatically at high pressure.)

(4) The formed green shape is baked at ~1000˚C. Baking is required to carbonize the binder. The resulting porous material has structural integrity and many industrial uses (e.g. as an insulation layer in the PBMR between the graphite lining and the pressure vessel inside wall).

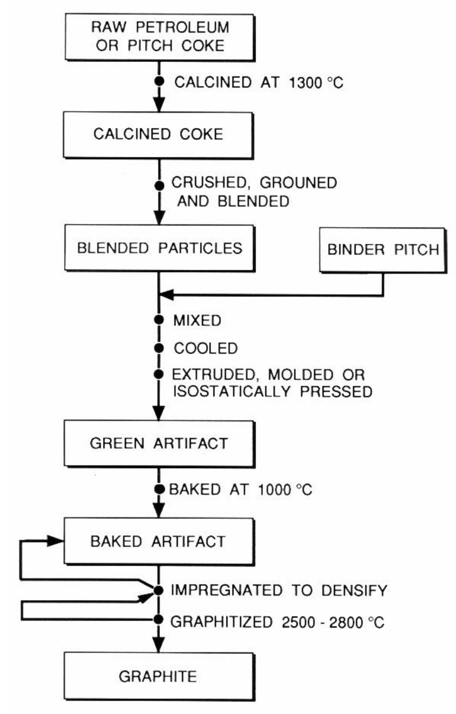
(5) Significant increases in the strength of the final graphite are obtained by reducing the porosity by means of impregnation-rebaking cycles prior to graphitization.

(6) Final conversion to graphite involving the development of three-dimensional order requires heat treatment to ~3000˚C.

(7) Commercial bulk graphites contain impurities as indicated by the ash content (see Table 4). For nuclear applications the impurities are subject to detailed specification: typically, the ash must be less than 300 ppm (parts per million). High purity is achieved through selection of pure raw materials (as with grade PGA) or purification with halogen agents either during (as with Gilsocarbon), or following, graphitization.

(8) Graphite is machined with standard machine tools. Purification can be achieved after machining.

Note the long processing time (Figure 11) of six to nine months. Bulk graphites are produced in a wide range of dimensions, grain sizes and types (see Table 5 and Table 6). Major producers of bulk graphite include Carbone, GrafTech International Ltd., Jilin, Poco, SGL Carbon, ShowaDenko, Tokai and ToyoTanso.




Some critical aspects of nuclear graphite manufacture:

- Raw material selection
  - Coke isotropy
  - Chemical purity
  - Stable long term availability
- Forming method
- Graphitization temperature
  - Develop adequate crystallinity
  - Minimize impurities
- Purification (if required)
- The typical manufacturing time for a nuclear graphite is six to nine months

**Figure 11 - The Major Processing Steps in the Manufacture of Nuclear Graphite**
(Courtesy T. D. Burchell, ORNL.)

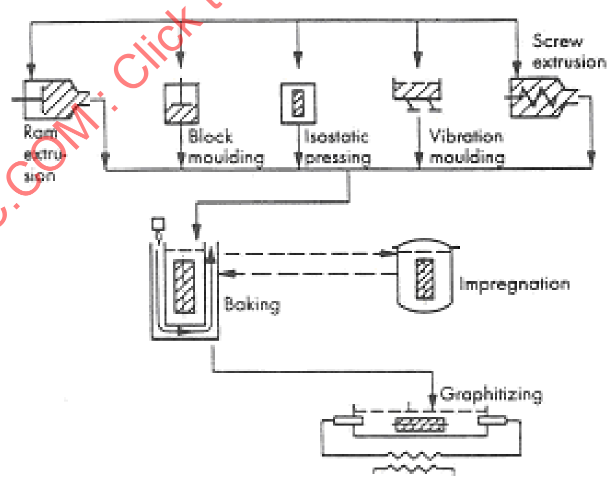



**Figure 12 - Forming Methods - Schematic [15]**

**Table 5 - Manufactured Graphite - Grain Size**

| | |
|---|---|
| Coarse grain | > 4mm |
| Medium grain | < 4mm |
| Fine grain | < 100 microns |
| Superfine grain | < 50 microns |
| Ultrafine grain | < 10 microns |
| Microfine grain | < 2 microns |
| * All sizes refer to 90% by weight passing the indicated size | |
| * ASTM C 709 Terminology | |

**Table 6 - Bulk Graphite Billet Sizes**

| | |
|---|---|
| **Extruded (medium & coarse grain)** | < 32 in. diameter x 88 in. |
| | < 24 in.x 48 in. rectangular cross section x 88 in. |
| **Molded, vibro-molded (medium grain)** | < 73 in. diameter x 73 in. and rectangular 27 in. x 18 in. x 92 in. |
| **Isomolded** | |
| Fine grain (<100 microns) | < 24 in. diameter x 72 in., < 16 in. x 16 in. x 80 in. or 12 in. x 24 in. x 80 in. |
| Superfine grain (<50 microns) | < 18 in. diameter, < 11 in. x 24 in. |
| Ultrafine (<10 microns) and microfine (<2 microns) grain | typically 6 in. x 6 in. |

## 4.2 Properties

It has already been noted that graphite is a relatively weak, porous, anisotropic, ceramic-like material. Graphite has high strength in-the-plane but the properties of bulk graphite are limited both by weak across-the-plane bonds, and by a pervasive connected porosity-microcrack system. Thus, bulk graphite is replete with irregular notches, the sources of which are summarized in Table 7. Bubbles and fissures from coke-making can be distinguished in the photomicrograph in Figure 13. The larger monochromic area labeled as pores are generated during the baking operation. The Mrozowski cracks which are created by the strains on cool-down after graphitization are illustrated in Figure 14.

**Table 7 - Bulk Graphite is Full of Notches which Arise in Manufacturing**

| |
|---|
| Bubbles formed during delayed coking (~500˚C) |
| Shrinkage fissures along domain edges during calcination cool-down (~1300˚C) and during baking cool-down (~1000˚C) |
| Bubbles formed during carbonization of binder (baking, ~1000˚C) |
| Bubbles formed during carbonization of impregnant (rebaking, ~1000˚C) |
| Mrozowski cracks formed during cool-down after graphitization (~3000˚C) |

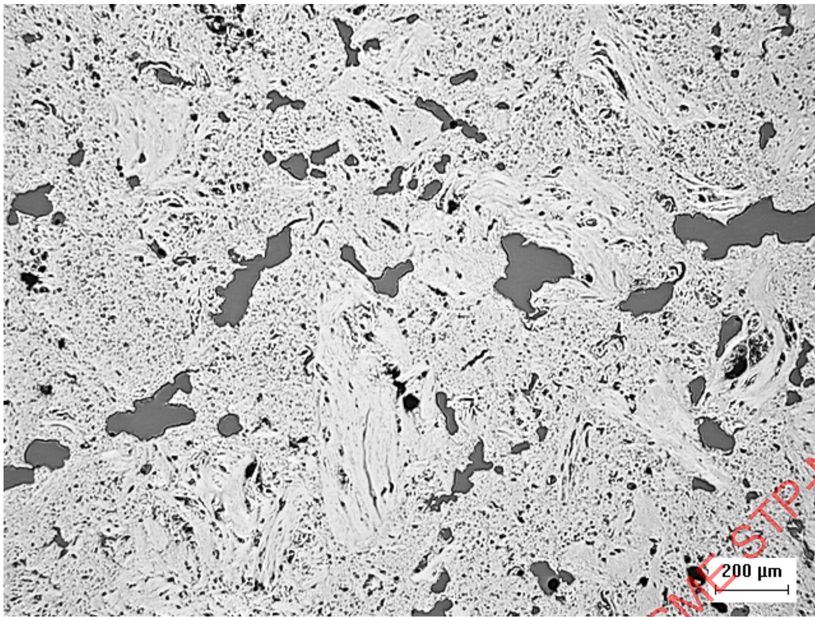
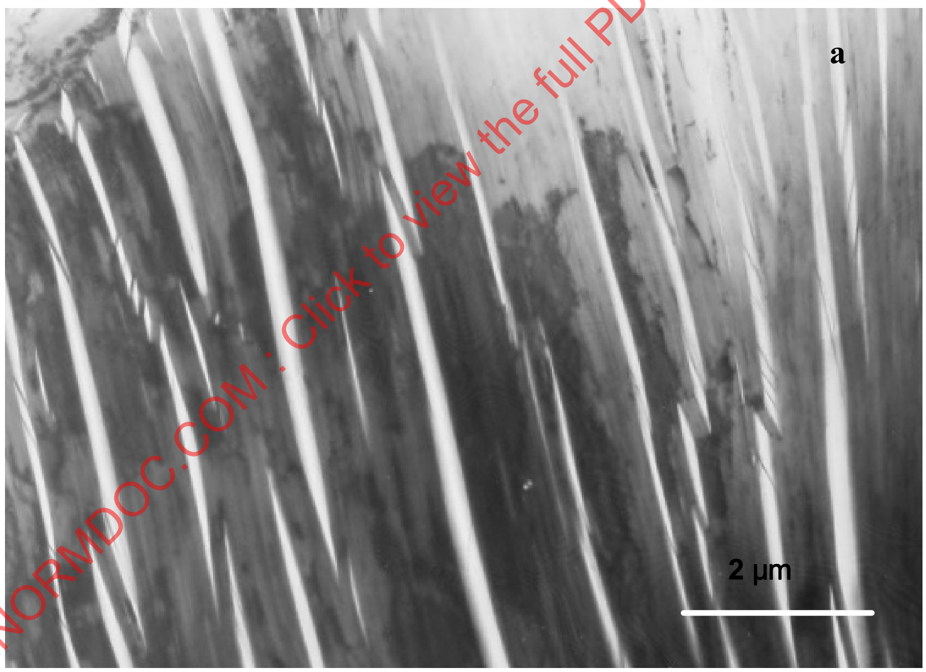



**Figure 13 - The Microstructure of Extruded Medium Grain Bulk Graphite**
(Courtesy: Doug Miller, GrafTech Holding Inc.)




- Microcracks were formed by cleavage along basal plane
- The length of the cracks varies from a few nm to more than 10 mm
- The width of the cracks varies from less than 50 nm to ~200 nm.

**Figure 14 - Transmission Electron Micrograph of PGA Graphite [16]**

Typical properties for a range of grades are recorded in Table 4. Those for nuclear grades are presented in Table 8 and Table 9. Also included in the latter table is a column summarizing the recently published ASTM specification (D 7219) for HTR isotropic and near-isotropic graphites.

**Table 8 - The Progression of Nuclear Graphite - Reactor Types**

| Start-Up, Year | Country | Reactor Type | Coolant | Graphite Grade |
|---|---|---|---|---|
| 1942–1960s | USA (USSR) | CP1, X10, B - N | Air, H20 | AGOT, KC - TSX |
| 1950–1970s | UK (France) | Magnox | CO2 | PGA |
| 1970–1989 | UK | Adv. Gas Reactor, AGR | CO2 | GCMB |
| 1970– | | AGR sleeves | | VNEA |
| 1980– | | AGR sleeves | | PPEA |
| 1964–1976 | UK | HTR-Dragon | He | Test-bed |
| 1966–1988 | Germany | Pebble Bed | He | GCMB-type |
| 1967–1989 | USA | HTR prismatic | He | H451 |
| 1991 | Japan | HTR prismatic | He | IG110 |
| 1990s | South Africa | PBMR pebble | He | NBG-18 |
| 1990s | USA, Russia | GT-MHR prismatic | He | H451-type,e.g. PCEA |

**Table 9 - The Progression of Nuclear Graphites - Graphite Grades**

| Property | AGOT | PGA | GCMB | VNEA | PPEA | H451 | IG110 | ASTM D 7219 Spec. |
|---|---|---|---|---|---|---|---|---|
| Max. grain size, mm | 0.8 | 0.8 | 1.7 | 0.8 | 0.8 | 1.6 | 10-micron, Avg | <4 |
| Bulk density, g/cc | 1.70 | 1.72 | 1.82 | 1.86 | 1.85 | 1.77 | 1.77 | >1.70 |
| CTE (RT-500˚C), ppm/C, wg/ag | 3.0/4.6 | 1.6/3.6 | 5.3/5.4 | 3.8/4.6 | 5.0/5.3 | 4.3/4.8 | 4.3/4.4 | 3.5-6.0/3.9-6.6<br>3.5-6.0/4.0-6.9 |
| CTE isotropy, (ag/wg) | 1.5 | 2.3 | 1.0 | 1.2 | 1.1 | 1.1 | 1.0 | 1.0-1.1<br>1.1-1.15 |
| Tensile strength, psi, wg/ag | 1435/1260 | 1145/855 | 2900/2900 | 2000/1600 | 3190/2755 | 2060/1655 | 3940/3705 | >2175/- |
| Ash, ppm | 740 | 100-2500 | 500 | 1000 | 10 | 50 | 20 | <300 |
| B, ppm | <1.0 | 0.1-0.7 | 0.2 | 0.5 | 0.5 | 2 | 1.4 | <2 |

Much has been published on the mechanical properties of bulk graphite. There are three issues to note:

(1) Graphite is brittle and the stress-strain curve is always non-linear. The tensile behavior of grade PGA is shown in Figure 15.

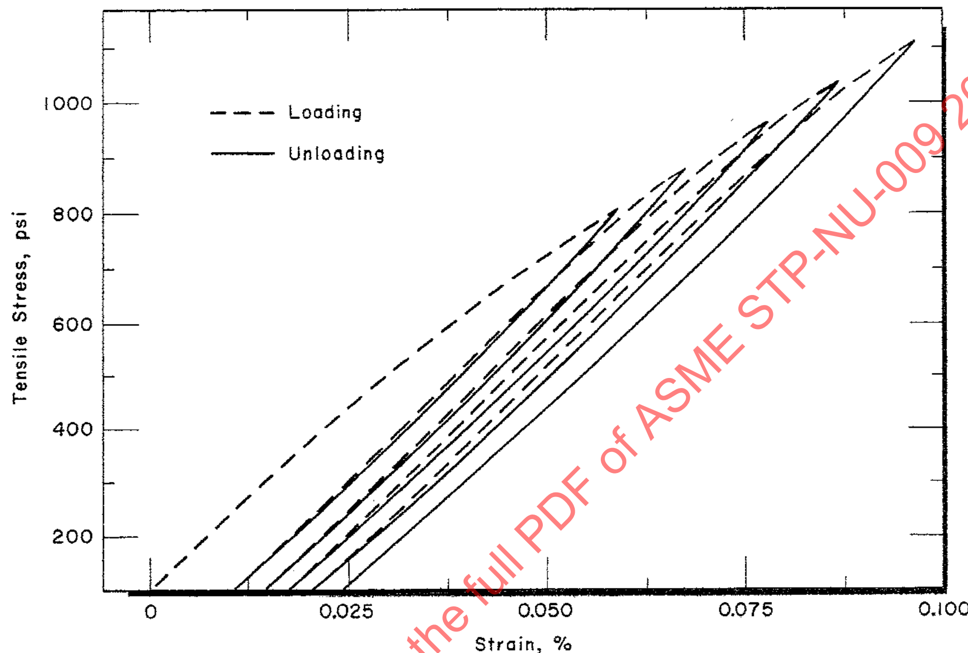



**Figure 15 - A Typical Tensile Stress-Strain Diagram for the Nuclear Grade PGA in the with Grain Direction [17]**

(2) The stress-strain curves have the same relative shape for a wide range of graphites (see Figure 16).

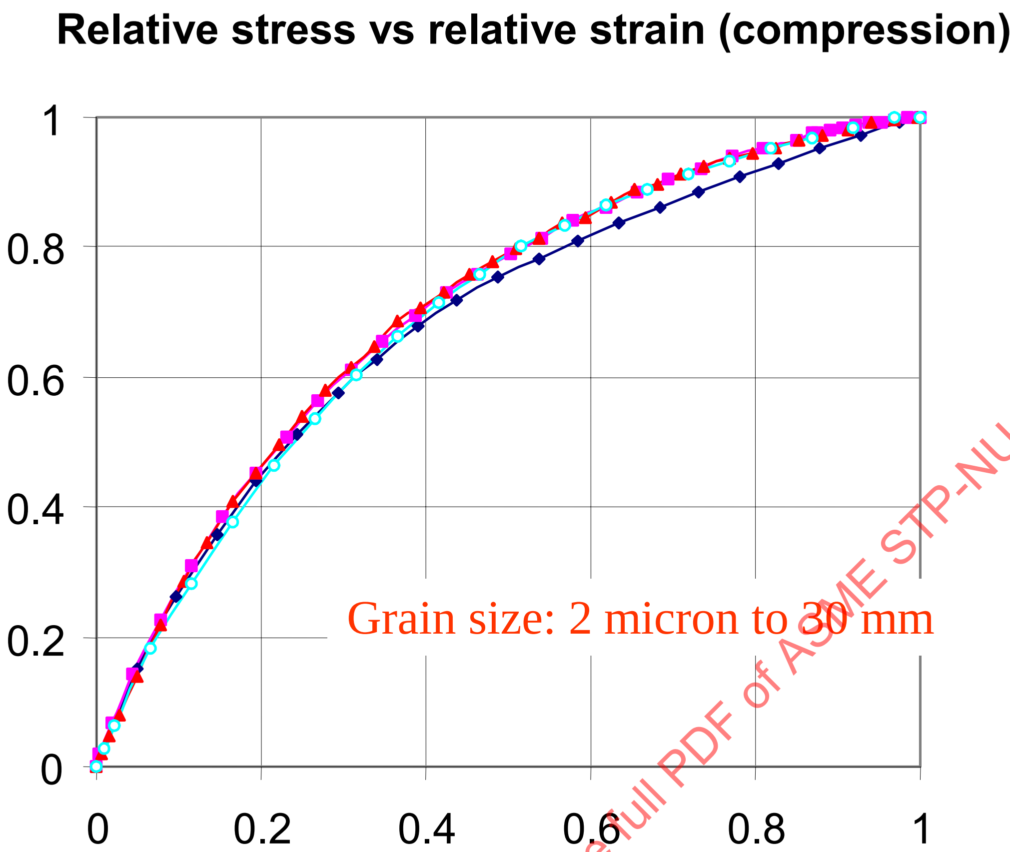



**Figure 16 - Stress-Strain Curves for a Wide Range of Graphites [18]**

(3) The wide variation in pore type, shape and size causes significant variation in mechanical properties both within blocks and between blocks. A coefficient of variation of 15% is not uncommon. Weibull statistics are used to describe populations with tails of unusually low magnitude (caused, for example, by uncharacteristic very large pores.) Designers find that a probabilistic approach is relevant when dealing with a material as variable as bulk graphite.

Graphite is unique among materials in that strength increases with increasing temperature. Tensile strength increases of 50% at 2000˚C are typical, limited only by the onset of plasticity (Figure 17). Of course, air and oxidizing gases must be excluded, otherwise graphite is gasified.

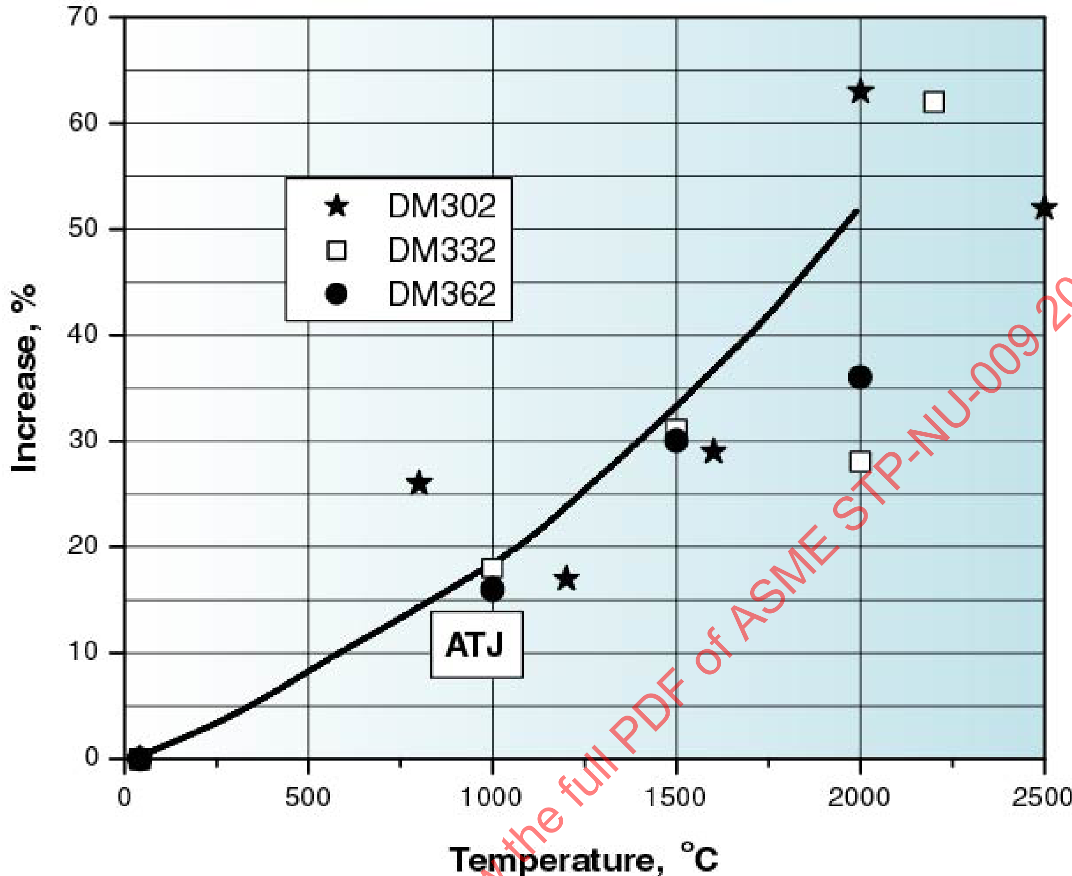



**Figure 17 - The Effect of Temperature on Tensile Strength [1]**

Oxidation susceptibility is conveniently measured in air. At temperatures below ~1200˚C, the oxidation is a mixed diffusion-chemical oxidant regime. Reaction typically occurs both on the outer extremities and throughout the material. Significant differences may arise between grades: certain impurities act as catalysts (see Figure 18). Carbon is much more reactive than graphite. Temperature has a marked effect on the gasification rate below ~1200˚C (see Figure 19). At higher temperatures, the oxidation rate is gas-phase-diffusion limited for all graphites and carbon loss from the outer extremities is dominant.

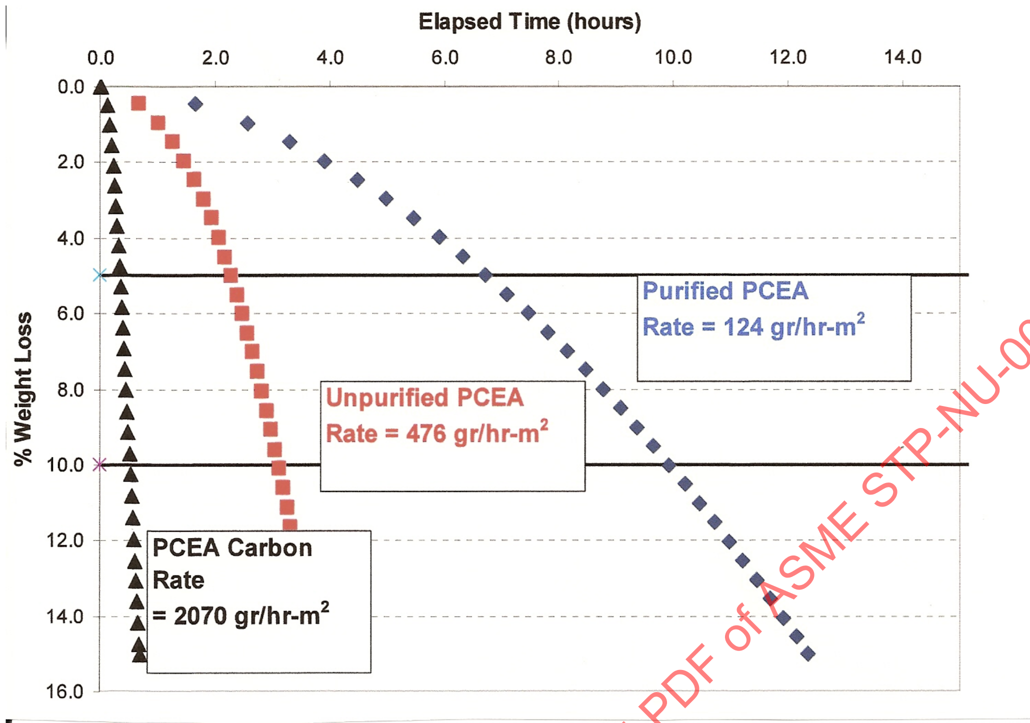



Figure 18 - Weight Loss in Flowing Air at 650˚C [19]

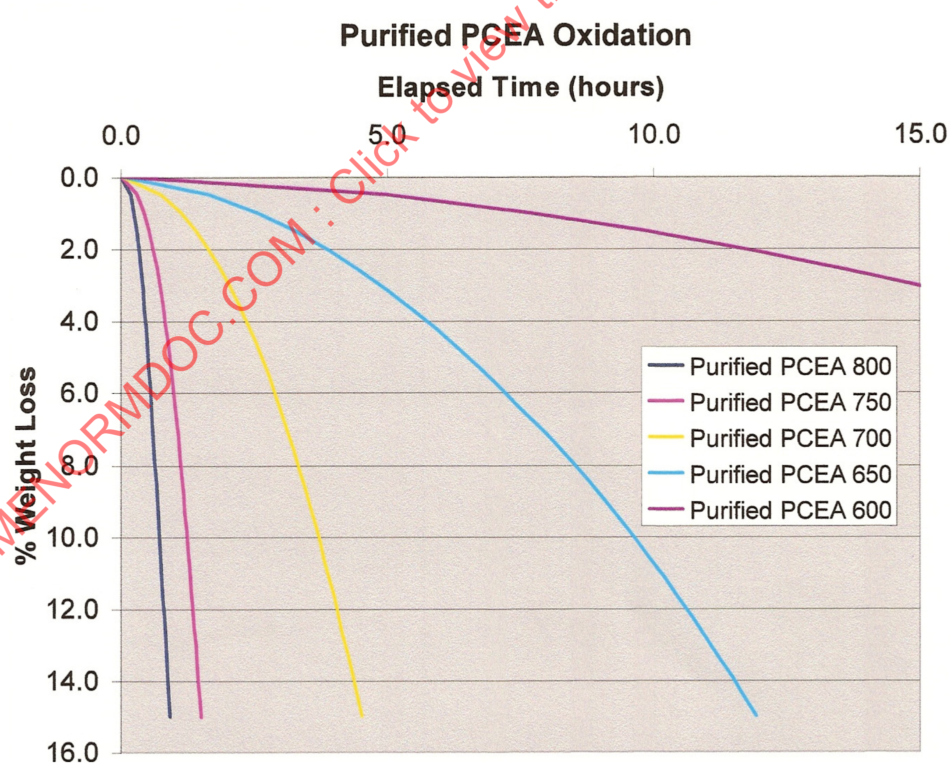
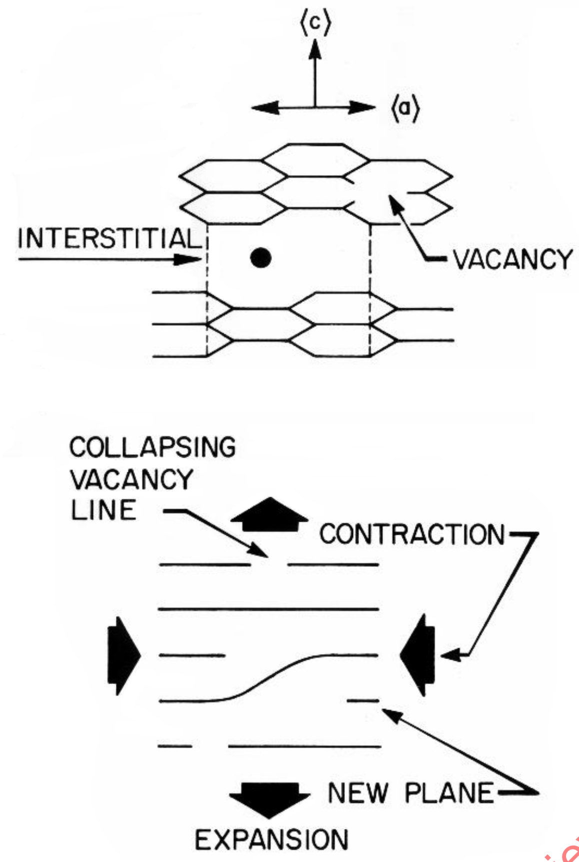



Figure 19 - The Effect of Temperature on Oxidative Weight Loss [20]

## 4.3 Irradiation Behavior

The mechanisms of the damage which graphite undergoes on neutron irradiation are well understood. However, the processes, summarized in Figure 20, have not been correlated with the properties of the pristine graphites. In other words, the behavior of a new graphite cannot be quantitatively predicted. Certain behaviors may be anticipated but this is insufficient basis for a designer. New graphites are subject to extensive accelerated irradiations, at several use temperatures, in a Materials Test Reactor (MTR) where progress is monitored by periodic measurements of specimen dimensions. As the fluence-temperature campaigns are completed the specimens are subjected to a battery of physical tests. MTR experiments on the new generation of candidate graphites such as those now in progress at the Oak Ridge National Laboratory (ORNL), the Idaho National Laboratory (INL) and the NRG-Petten (Holland) are multi-year, multi-million-dollar programs. (For more on the new generation of nuclear graphites, see Section 4.)



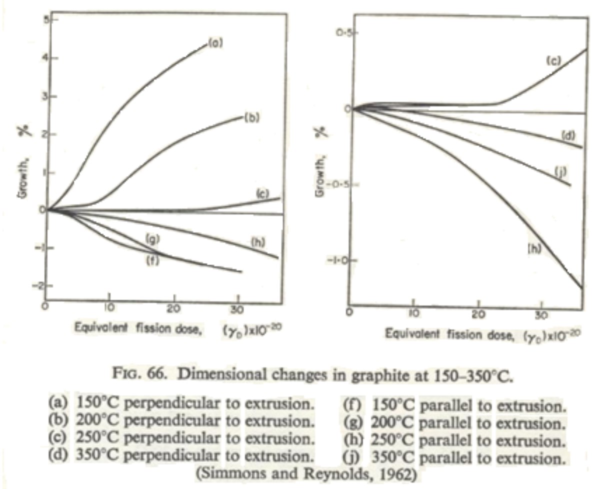

- Crystal undergoes c-axis expansion and a-axis shrinkage
- Damage accumulates rapidly at $T_{irr}$ <400˚C (lack of vacancy mobility)
- Crystal changes interact with structure (porosity) in graphite
- Low temperature against grain swelling and with grain shrinkage. Against grain swelling saturates and shrinkage behavior observed
- High temperature ($T_{irr}$ >300˚C) shrinkage with turnaround to swelling at higher doses
- Higher dose turnaround into volume swelling due to incompatibility of crystal strains causing new pore generation
- Defect structures impede basal plane dislocation movement and thus strength and modulus increase rapidly
- Physical properties affected by structural changes

**Figure 20 - Irradiation Damage Mechanism**
(Courtesy: T. D. Burchell, ORNL.)

A single neutron with an energy of 2 Mev causes 60 primary knock-on carbon atoms, 350 secondary knock-on atoms and a net movement of 20,000 carbon atoms. Yet the graphite survives long enough to be practically useful because of complementary thermal and neutron collision annealing effects as well as irradiation creep.

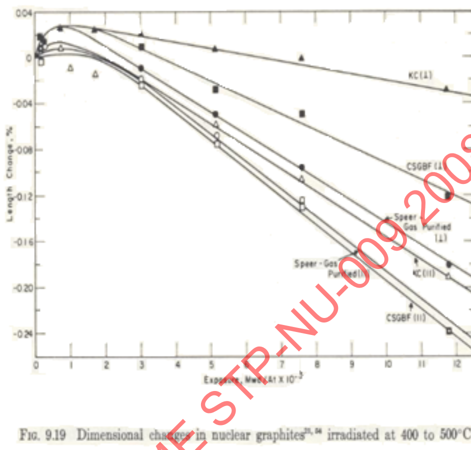
The dimensional changes of relatively anisotropic graphites used in the Magnox and Hanford reactors (see Table 8 and Table 9) are shown in Figure 21. Clearly evident is widely different behavior with expansion in the against-grain direction and shrinkage in the with-grain direction. The importance of exposure temperature is evident with expansion inversely related to the temperature. At higher temperatures (400˚C–500˚C) an initial expansion is followed by an essentially linear decline. The behavior with and against grain is very different.

$T_{irr}$ = 150-350 °C




From J.H.W. Simmons (1965)

$T_{irr}$ = 400-500 °C




From R.E. Nightingale (1962)

**Figure 21 - Low Dose, Low Temperature Dimensional Changes**

Grades of increased isotropy such as H451, GCMB and PPEA were developed for the higher operating temperature HTR and AGR reactors of the 1970s and 1980s. The dimensional changes associated with these grades (see Table 9 for pristine properties) are exemplified by the behavior of H451 at 600˚C and 900˚C (see Figure 22 and Figure 23). The length changes in the two grain directions are almost parallel, thus presenting differential strain effects in the reactor core which can be managed. There are initial shrinkages culminating in a maximum which is defined as turnaround. The graphite is now expanding and growth eventually crosses the origin (defined as crossover). Expansion continues and the physical properties deteriorate rapidly. Reactor core service life is defined somewhere between turnaround and crossover.