STP/PT-004

# IMPREGNATED GRAPHITE FOR PRESSURE VESSELS



ASME STANDARDS TECHNOLOGY, LLC

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# IMPREGNATED GRAPHITE FOR PRESSURE VESSELS



*Prepared by:*

The Special Working Group on Graphite Pressure Equipment

ASME STANDARDS TECHNOLOGY, LLC

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ASME Standards Technology, LLC
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# TABLE OF CONTENTS

## List of Tables



## List of Figures

## List of Equations

# FOREWORD

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## ABSTRACT

Impregnated graphite (also called impervious graphite) is a material that has been in industrial use for the past 60 - 70 years. The primary industrial use has been in the construction of chemical processing equipment where the exceptional corrosion resistance and high thermal conductivity of graphite is particularly advantageous. Typical applications include the manufacture of pharmaceuticals and phosphate fertilizer, steel pickling, processing of chlorinated organics, flue gas treatment, HCl and $H_2SO_4$ production and recovery, plus the manufacture of chemical intermediates.

The impervious graphite used for the construction of graphite pressure vessels is a composite material, consisting of "raw" graphite that is impregnated with a resin using a tightly controlled pressure/heat cycle. The interaction between the raw material and the resin is the determining factor when considering the design characteristics of the material. The design characteristics include the strengths (flexural, compressive, tensile), porosity, coefficient of thermal expansion, thermal conductivity, and ultimately the safe operating life of the vessel.

Proposed new pressure vessel rules will apply to the impregnated material only. There are two main reasons for this. First, the raw material is porous in nature and cannot be used as a pressure-containing material. Second, the resin impregnation process is a major factor when considering the properties of impregnated graphite. To consistently meet the minimum design values, the resin impregnation process must be tightly controlled. The resin impregnation processes used today have been developed over a 70-year period. The essential variables of the process have been defined and apply universally to all manufactures of impervious graphite equipment. By verifying the essential variables, it is possible to assign a lot number to all certified materials. The manufacturer's control of this process is assured through meaningful and consistent test data. The long and successful worldwide experience with impregnated graphite vessels demonstrates that impregnated graphite vessels are safe and reliable under various aggressive service conditions.

This report presents a view of current best practices and recommendations for development of new rules. This paper describes many of these rules and much of the logic that has gone into creating the proposed section, and it is intended to provide a basis for the development of consensus standards addressing the use of impregnated graphite for ASME Section VIII Division 1 pressure vessels. It is the hope of the committee that this document will help to provide a strong background of information supporting continued efforts directed at inclusion of the proposed part UIG in Section VIII.

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# 1 INTRODUCTION

Graphite is a form of carbon possessing good corrosion resistance. Impregnated graphite (also called impervious graphite) is a material that has been in industrial use for the past 60 to 70 years. The primary industrial use has been in the construction of chemical processing equipment where the exceptional corrosion resistance and high thermal conductivity of graphite is particularly advantageous. It is usual for this equipment to remain in service for many years.

Impregnated graphite is commonly used for chemical processes involving sulfuric acid ($H_2SO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), phosphoric acid ($H_3PO_4$), and hydrofluoric acid (HF). Typical applications include the manufacture of pharmaceuticals and phosphate fertilizer, steel pickling, processing of chlorinated organics, flue gas treatment, HCl and $H_2SO_4$ production and recovery, and the manufacture of chemical intermediates.

Major components of chemical process equipment are manufactured from impervious graphite. These include tubes for heat exchangers and solid blocks. Components, such as tubesheets, headers, and nozzles are obtained by machining impervious graphite to size.

Numerous companies have been engaged in the manufacture of impervious graphite equipment and have produced over 50,000 heat exchangers on a worldwide basis. Some companies that have been or are currently engaged in the manufacture of new impervious graphite equipment are: Union Carbide, Carborundum, SGL Carbon, Carbone Lorraine, Kearney Industries, Ralph Coidan, and Metaullics. Typical trade names in use today are: Diabon, Graphilor, Impervite, and Karbate.

Currently there are no rules in the ASME Boiler and Pressure Vessel Code for design and construction of graphite pressure vessels. Many of the older graphite pressure vessels were designed and manufactured to the manufacturer's in-house standards. However, requirements for pressure equipment made of graphite are included in some of the European and Asian pressure vessel codes. Most of the more recently produced graphite pressure vessels in the United States are based on the design and construction requirements of the German pressure vessel code AD Merkblatt N2.

ASME has established a Special Working Group on Graphite Pressure Equipment (SWG-GPE) to develop rules for design and construction of impregnated graphite pressure equipment. The objective is to include these rules as Part UIG of Section VIII, Division 1 (Part UIG is the designation of the requirements for impregnated graphite intended for publication in Section VIII Division 1 of the Boiler and Pressure Vessel Code). These rules will incorporate generally accepted international practices that have resulted in reliable and safe impregnated graphite pressure equipment.

# 2 IMPREGNATED GRAPHITE

## 2.1 History

Graphite is a naturally occurring form of carbon. Edward G. Acheson accidentally synthesized graphite while he was performing high-temperature experiments on silicon-carbide. At about 4,150°C (7,500°F) he found that the silicon in the silicon-carbide vaporized, leaving the carbon behind in graphitic form. A patent for the manufacture of graphite was granted to Acheson in 1896, and commercial production started in 1897[1].

Graphite has been used in the chemical and metallurgical industries since the time of Sir Humphrey Davy; circa 1800. However, porosity (on the order of 25%) prevented the use of graphite in many chemical process applications. In the 1930s, the then National Carbon Company developed a process (impregnation) to make the graphite impervious to fluids. The imperviousness is obtained by filling the pores of the graphite material with thermosetting resins, such as phenolics, furans and epoxies, during a vacuum/pressure impregnation process.

Today, major elements of process equipment are manufactured from impregnated graphite. These elements include tubes, nozzles and cylinders, solid blocks, plates, tubesheets, and more. The impregnation process has allowed graphite with its excellent corrosion resistance and thermal conductivity properties to be used in chemical process equipment under pressure, such as impervious graphite shell and tube heat exchangers (see Figure 1). Typical applications include condensing and evaporating acids, such as hydrochloric and phosphoric. Over the past 60 years, improvements in the impregnation process allowed shell and tube heat exchangers to increase in size from 7-tube units 9 ft long to 2,125 tube units 27 ft long.

## 2.2 Manufacturing of Impregnated Graphite Products

The materials used in manufacturing graphite are fillers (petroleum coke, natural and synthetic graphite) binders (coal tar pitch), and additives. Their conversion into machined impervious graphite material for process equipment involves the following steps:

- Prepare the raw materials by grinding, sorting and blending.
- Mix the raw materials to form a molding flour.
- Compress the molding flour into tubes and blocks.
- Bake the formed components at temperatures of about 1,800°F (980°C). Baking the shaped components (to carbonize the binder) produces a porous solid material whose pore structure changes only very slightly in the graphitizing process.
- Graphitizing is carried out in graphitizing furnaces at 4,700 to 5,400°F (2,595 to 2,980°C). This process rearranges the carbon-rich raw materials and carbonized binders at a molecular level into graphite. The resulting material exhibits high thermal shock resistance and conductivity, as well as strong resistance to chemical attack.
- Graphite is machined with standard machine tools into process equipment components, such as heat exchanger tubes, heat exchanger blocks, tube sheets, and headers.

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[1] Impervious Graphite for Process Equipment, Parts 1 and 2, Chemical Engineering, February 18 and March 18, 1974.

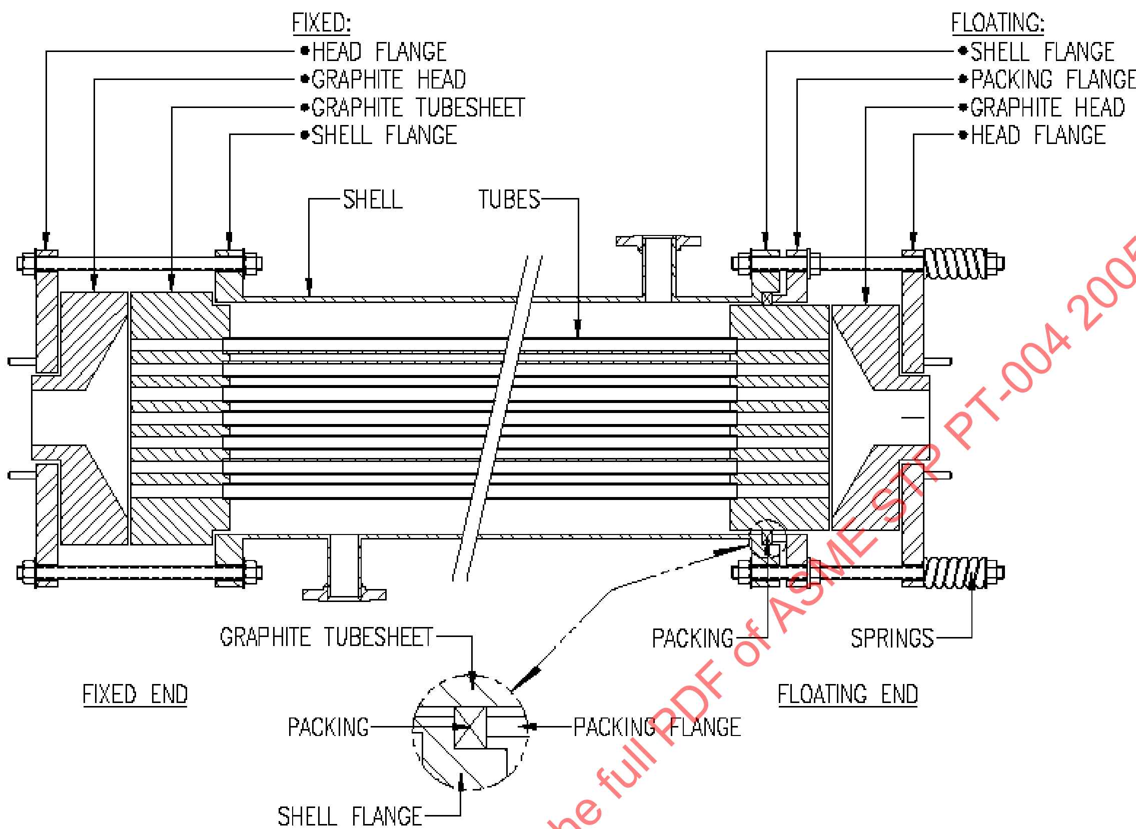



**Figure 1 - Typical Graphite Shell and Tube Heat Exchanger**

- The impermeability of graphite is achieved by impregnating the graphite components with resin. The resin is forced into the pores by a vacuum/pressure process and subsequently cured at a predetermined temperature. This also provides a significant increase in strength.
- The bonding of joints in graphite components is termed cementing. The cement typically consists of a corrosion resistant resin binder, graphite powder, and a catalyst. Stresses at the cemented joint are minimized by using an appropriate joint design. The cementing operation is monitored and controlled by the manufacturer.

A typical flow diagram for the manufacture of impregnated graphite products is shown in Figure 2.

## 2.3 Material Specifications

Specifications exist for graphite and for impregnating agents; however, there are no published specifications for impregnated graphite. Impregnated graphite is made up of different combinations of graphite and impregnating agents that are combined in a specified process to make the composite material. Also, some grades may be more suitable for certain applications (service conditions) than other grades. The graphite manufacturing process is specified by the manufacturer and is proprietary. The “specified process” is a listing of each step required to produce a specific “grade” of impregnated graphite. It includes such items as the grade of graphite, resin, vacuum, pressure, and any other steps needed to produce the desired grade of impregnated graphite.

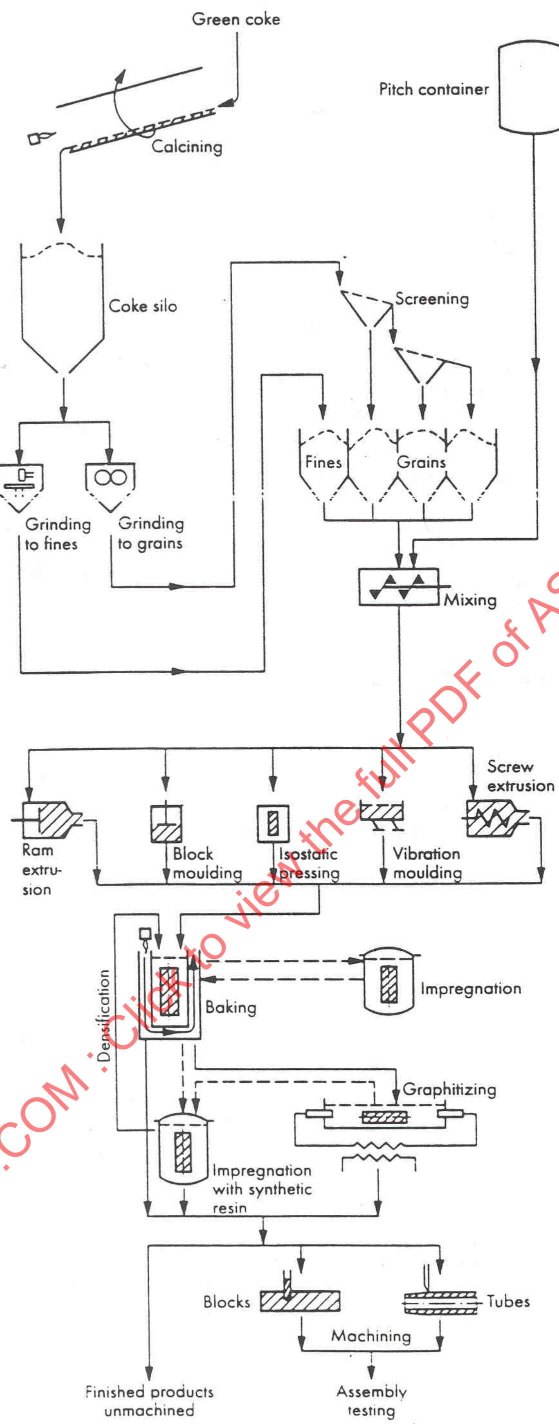





**Figure 2 - Typical Flow Diagram for Manufacture of Impregnated Graphite Products**
(from Würmseher [2] figure 3)

Graphite is porous and must be impregnated with resin to make it impervious to gases and liquids; therefore, only impregnated graphite is suitable for construction of pressure vessels and components. However, the resin used for impregnation has a significant effect on mechanical properties of graphite. The impregnation cycle and resin type may vary from manufacturer to manufacturer and also for each grade of the impregnated material the vessel manufacturer produces; therefore, the impregnation process must be tightly controlled to ensure that the material meets the specified properties.

The graphite vessel manufacturer is required to prepare a Certified Material Specification (CMS) that includes all the essential and nonessential variables as defined in the proposed Part UIG. The material is then tested in accordance with the procedures and other requirements of the proposed Part UIG and shall meet the mechanical properties listed in Table 1. (See Qualification of Certified Material Specifications in this report for analysis of test data.)

**Table 1 - Required Properties of Certified Material**

| | Tube[a] Material | Block[a] Material | Compound[b] Material | Cement[c] Material |
|---|---|---|---|---|
| Min. tensile strength at room temp. | 3,800 psi (26.2 MPa) | 1,500 psi (10.3 MPa) | 1,500 psi (10.3 MPa) | 1,500 psi (10.3 MPa) |
| Min. tensile strength at max. design temp. | 3,000 psi (20.7 MPa) | 1,200 psi (8.3 MPa) | 900 psi (6.2 MPa) | 900 psi (6.2 MPa) |
| Min. flexural strength | 5,700 psi (39.3 MPa) | 2,500 psi (17.2 MPa) | 2,500 psi (17.2 MPa) | N/A[d] |
| Min. compressive strength | 10,000 psi (69 MPa) | 4,500 psi (31 MPa) | 4,500 psi (31 MPa) | N/A[d] |
| Max. coefficient of permeability | $4.5 \times 10^{-6}$ in$^2$/s ($2.9 \times 10^{-3}$ mm$^2$/s) | $4.5 \times 10^{-6}$ in$^2$/s ($2.9 \times 10^{-3}$ mm$^2$/s) | $4.5 \times 10^{-6}$ in$^2$/s ($2.9 \times 10^{-3}$ mm$^2$/s) | N/A[d] |

[a]Resin impregnated graphite.

[b]Resin bonded graphite.

[c]Resin with graphite filler and catalyst.

[d]N/A, not applicable.

# 3 PROPERTIES OF IMPREGNATED GRAPHITE

## 3.1 General

Typical properties of impregnated graphite important in the design of graphite components are given in Table 2. Table 2 also gives a comparison of the mechanical and physical properties of impregnated graphite with those of the more conventional materials used in pressure vessels.

**Table 2 - Properties of Impregnated Graphite and Other Materials**

| Properties | Typical Properties of Impregnated Graphite (Tube)[a] | SA-516, Gr. 70[b] | SA-240, Type 316L[b] | Tantalum[c] |
|---|---|---|---|---|
| Tensile strength, psi | 4,060 - 4,790 | 70,000 (min.) | 70,000 (min.) | 8,700 - 14,500 |
| Flexural strength, psi | 6,500 - 8,700 | Not specified | Not specified | Not specified |
| Compressive strength, psi | 10,900 - 12,300 | Not specified | Not specified | Not specified |
| Modulus of elasticity, psi | $36 \times 10^5$ - $39 \times 10^5$ | $29 \times 10^6$ | $28 \times 10^6$ | $27.5 \times 10^6$ |
| Poisson's ratio | 0.2 - 0.25 | 0.3 | 0.3 | 0.35 |
| Elongation at break, % | 0.15 - 0.3 (typ.) | 21 - 27 (min.)[d] | 40 (min.)[d] | 15-25 (typ.) |
| Thermal conductivity, Btu/hr ft °F | 46.2 | 31.6 | 10.1 | 31.0 |
| Coefficient of thermal expansion, in/in/°F | $2.4 \times 10^{-6}$ | $7.5 \times 10^{-6}$ | $10 \times 10^{-6}$ | $3.6 \times 10^{-6}$ |
| Specific heat Btu/lb°F | 0.24 | 0.12 | 0.12 | 0.03 |

[a]Carbon and Graphite Materials to Withstand Highly Corrosive Environment in Pressure Vessels and Chemical Process Equipment, SIGRI Electrographite, GmbH (*English translation of the title from the German publication*)[2].

[b]ASME Boiler and Pressure Vessel Code, Section II, Part D, 2004 Edition[3].

[c]*Marks Standard Handbook for Engineers*[4].

[d]Elongation in 2 in. (50 mm) gage length.

The factors governing the mechanical properties of impregnated graphite are:

- The inherent strength of graphite
- Distribution and size of pores
- The characteristics of the resin and the impregnation process

The mechanical properties of the graphite, such as flexural and tensile strength, compressive strength, and permeability, are improved by resin impregnation. The reason for this strength increase is shown in Figure 3. Microcracks, which according to Griffith [5] are responsible for crack initiation in the material, are filled with resin. A resin bridge is formed, which prevents the crack from opening and thus the propagation of the crack. Because of the higher ductility of the synthetic resin (and lower modulus of elasticity), as compared to graphite, the localized stresses at the notch are reduced.

Another feature of graphite is the influence of temperature on tensile strength. Unlike most other materials, the tensile strength of non-impregnated graphite does not decrease with temperature, but increases markedly up to about 4,530°F (2,500°C) (see Figure 4). At temperatures at which impregnated graphite is normally used [400°F (200°C)], the slight increase in tensile strength is overridden by a much greater decrease in the modulus of elasticity of the synthetic resin as the temperature increases. Figure 4 shows the reduction of the tensile strength of impregnated graphite as the temperature increases.

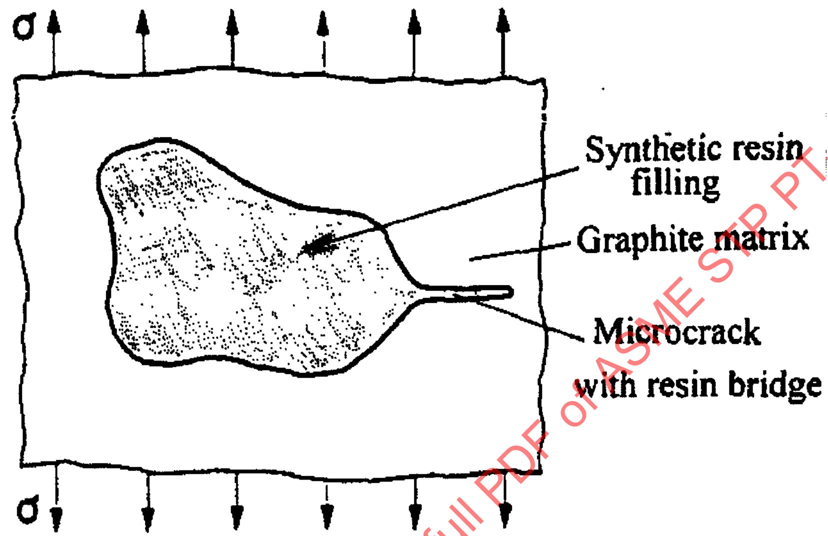



**Figure 3 - Schematic View of Resin-Filled Pore and Microcracks Under Stress**
(from Würmseher [2] figure 10)

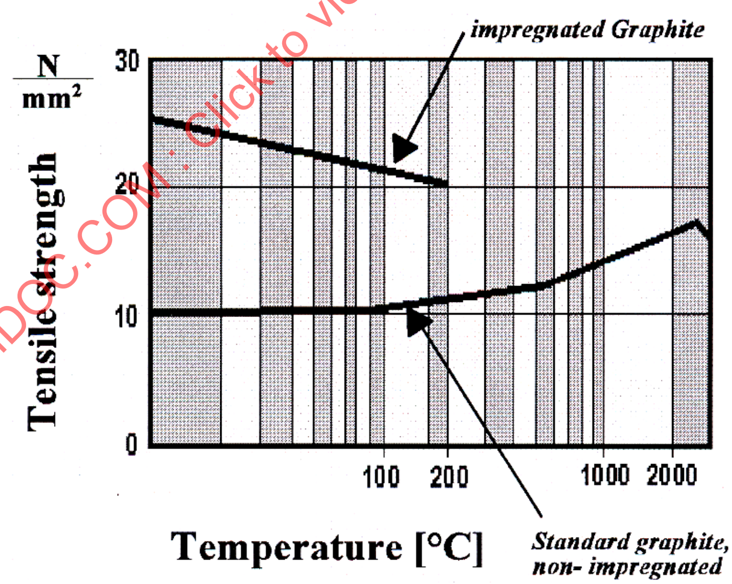



**Figure 4 - Tensile Strength of Impregnated Graphite and Nonimpregnated Graphite as a Function of Temperature**
(from Würmseher [2] figure 9)

## 3.2 Union Carbide Tests

In the mid 1970s, Union Carbide performed a series of tests to confirm the validity of the design margin of 5 that has been used for impregnated graphite since the 1930s. Hundreds of tests were performed over the temperature range for the graphite in use. These test results are shown in Figure 5 and Figure 6. They compare the measured stress at failure and the design stress. At that time, Union Carbide used a design stress of 400 psi (2.76 MPa) at all temperatures. The ratio of the measured stress at failure to the design stress exceeded 5:1 even at 340° F (170° C). The mechanical properties of impregnated graphite have increased since the 1970s.

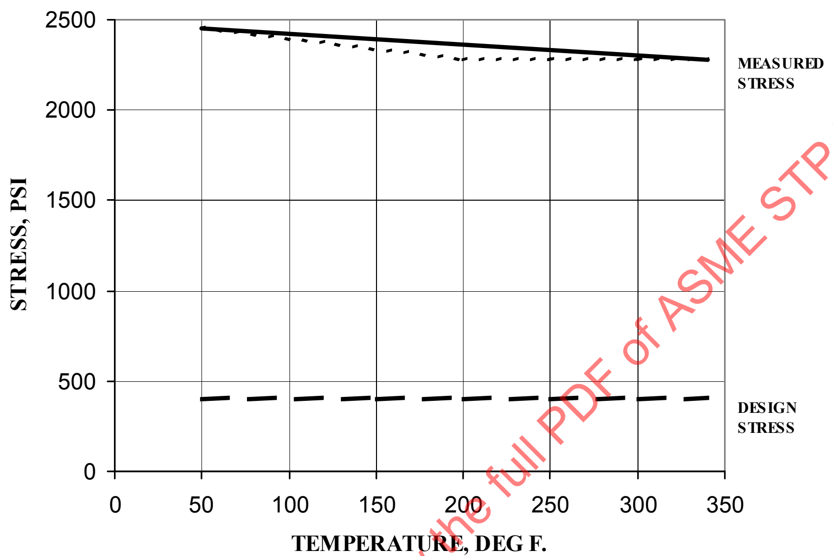



**Figure 5 - Tensile Strength vs. Temperature Union Carbide Tests**

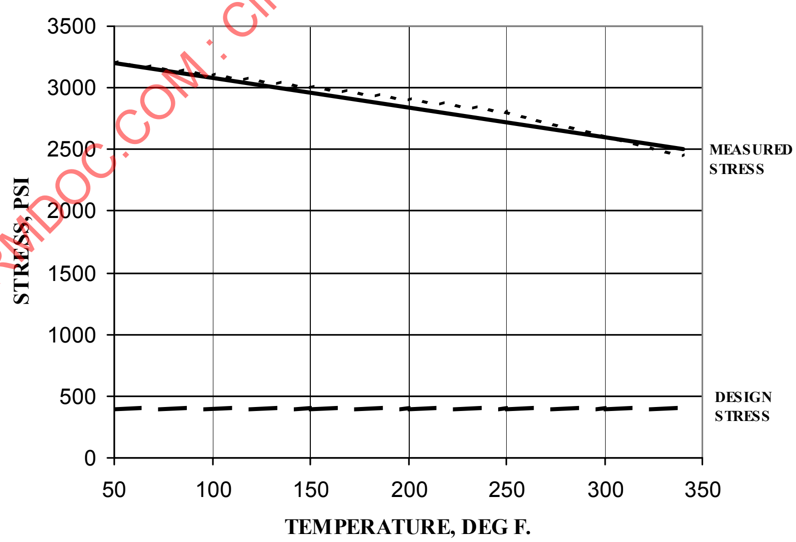



**Figure 6 - Flexural Stress vs. Temperature**

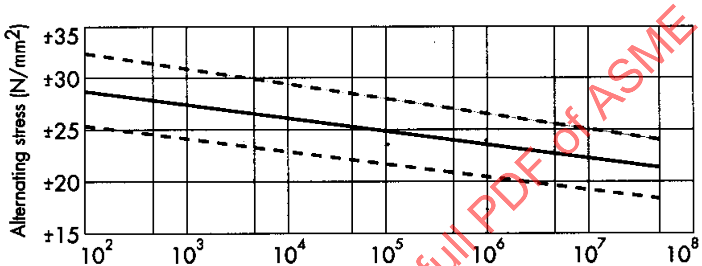
## 3.3 Creep

Creep is defined as plastic flow under stress. Graphite displays extremely low creep at room temperature; its flow characteristics being comparable to those of concrete. Graphite is not perfectly elastic, even at room temperature, and yields plastically under stress as the stress is increased. The stress-strain curves for graphite are not linear, and there is a residual strain in the material after stressing, which increases as the maximum stress is increased. However, this plastic straining is not generally considered to be creep. Genuine creep, over periods up to several hours has been observed in graphite, but only at extremely high temperatures, such as 3,090°F (1,700°C) and above, which is not applicable or considered in the scope of the proposed Part UIG.

## 3.4 Fatigue Strength of Impregnated Graphite

### 3.4.1 Data from SGL Carbon Group

Typical fatigue strength of impregnated graphite under reversed bending stresses is shown in Figure 7.




Number of cycles, N (Note: 1 N/mm2 = 1 MPa)

**Figure 7 - Typical Fatigue Strength of Process Equipment Impregnated Graphite Under Alternating Bending Stresses**
(from SGL Brochure M, 2/97)

### 3.4.2 Fatigue Tests by Hoechst

Fatigue tests were performed by the Hoechst Group in Germany on three impregnated graphite tubes with $D_o$ = 1.25 in. (32 mm), $D_i$ = 0.85 in. (28 mm), and length L = 27.3 in. (700 mm). The tubes were fixed at one end and the other end was subjected to fatigue loads at 20 to 25 cycles/sec. The following table summarizes the test results on these tubes.

**Table 3 - Hoechst Fatigue Tests**

| Alternating Stress at Fixed End, psi ($N/mm^2$) | Maximum Fatigue Cycles, N | Comments |
|---|---|---|
| 1,450 (10) | $7 \times 10^6$ | No damage observed |
| 2,900 (20) | $7 \times 10^6$ | No damage observed |
| 4,350 (30) | $7 \times 10^6$ | No damage observed |
| 5,800 (40) | $7 \times 10^6$ | No damage observed |
| 7,250 (50) | $0.09 \times 10^6$ | Failure of one test specimen |
| | $7 \times 10^6$ | Failure of second test specimen |
| 8,700 (60) | $1.9 \times 10^6$ | Failure of third test specimen |

These test results indicate that when stressed at sufficiently low stresses, impregnated graphite exhibits excellent fatigue life. However, its low modulus of elasticity results in higher strain per unit of stress than the materials used for metallic vessels. The proposed design margin of 6 on tensile strength results in low allowable design stresses for graphite components (see section 4.4) so that fatigue is not a concern.

## 3.5 Modulus of Elasticity

Impregnated graphite has a low modulus of elasticity as compared to ferritic materials (see Table 2).

## 3.6 Notch Sensitivity of Impregnated Graphite

There has been very little research on the subject of notch sensitivity of impregnated graphite. However, several published papers [11, 12] discuss notch sensitivity and stress concentration factors in non-impregnated graphite. Tucker [11] discusses notch sensitivity, n, in brittle and in semi-brittle materials. Tucker defines notch sensitivity as follows:

$$n = \frac{\sigma_u}{K_t \sigma_n}$$

where

$\sigma_u$ = stress required to break an unnotched specimen

$\sigma_n$ = the observed mean stress in the notch section at failure

$K_t$ = theoretical stress concentration factor for the geometry of the test specimen

**Equation 1 - Notch Sensitivity**

Notch sensitivity depends on the curvature at the root of the notch and tends to be an asymptotic value for large radii at the root of the notch. Figure 8 shows the assumed profile of the doubly notched plate for the analysis. Figure 9 plots the notch sensitivity, n, vs. root radius for three defect sizes, c, and three notch depths, t. It shows that the notch sensitivity, n, tends to become an asymptotic value when the notch root radius is in the range of about 1/4 in. (6.3 mm) to 1/2 in. (12.7 mm).

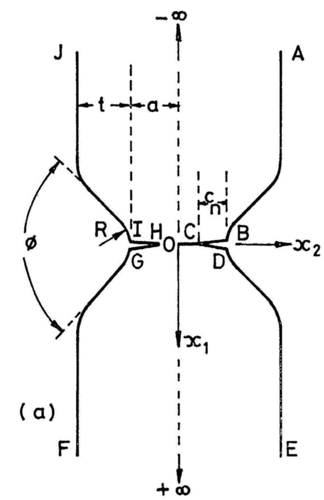



**Figure 8 - The Assumed Profile of a Doubly Notched Plate**
(From Tucker [11] figure 1)

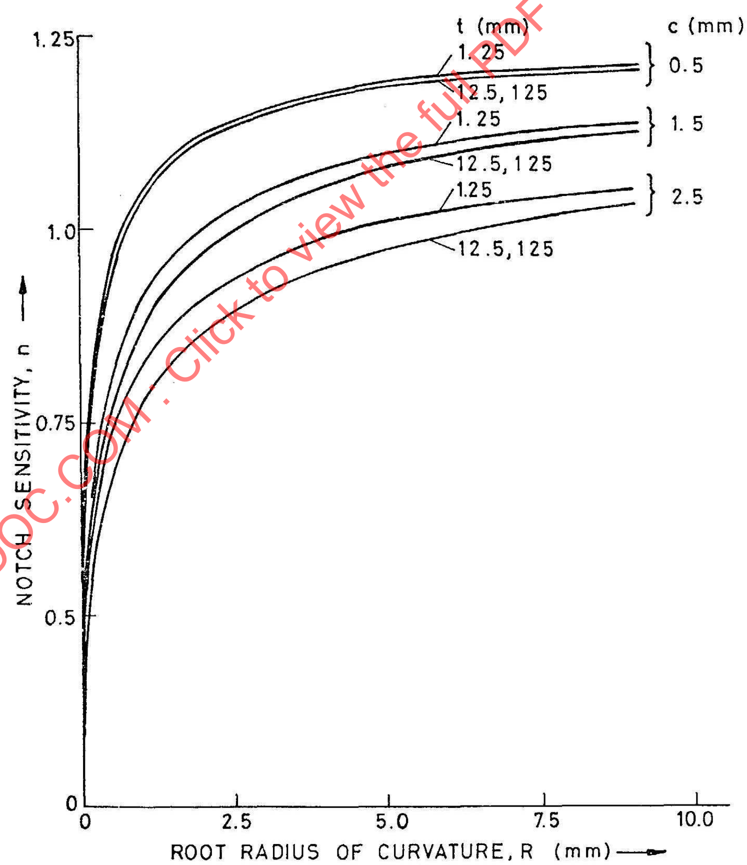



**Figure 9 - Notch Sensitivity vs. Root Radius for Three Defect Sizes, c, and Three Notch Depths, t**
(From Tucker [11] figure 4)

Bazaj and Cox [12] determined theoretical and experimental stress concentration factors, $K_t$ and $K_e$, in grooved nonimpregnated graphite tension test specimen.

$$K_e = 0.143r^{-0.469} + 0.757$$

where

r = notch root radius

**Equation 2 - Experimental Stress Concentration Factor**

They found the experimental stress concentration factor, $K_e$, to be dependent upon the maximum grain size in the test specimen.

Bazaj and Cox also determined theoretical and experimental notch sensitivity indices, $q_t$ and $q_e$. They stated that in most cases the experimental notch sensitivity values $q_e$, will give a better prediction.

$$q_e = \frac{0.943 \times 10^{-3.87r} - 0.097}{0.143r^{-0.469} - 0.243}$$

where

r = groove radius

**Equation 3 - Experimental Notch Sensitivity Index**

Because of the resin, impregnated graphite is likely to be less sensitive to notches than non-impregnated graphite. The industry experience by the SWG-GPE members is that the simple rule "No sharp inside corners" and rounding the inside corners to 1/4 in. (6.3 mm) or larger radius virtually eliminates the risk of crack initiation in those areas of impregnated graphite components.

## 3.7 Corrosion Resistance

Impregnating graphite with resins to reduce its porosity invariably produces a composite material with unique corrosion resistance and thermal stability characteristics, especially when compared to the original characteristics of the graphite. The selection of the most appropriate grade from the many available and use in combination with the most effective resin is perhaps the most crucial aspect of Graphite Process Equipment design. In essence, the chemical resistance of the composite part is determined by how long the resin will maintain its imperviousness. This is greatly affected by the size and availability of the porosity within the graphite part, which to a large degree determines how well the selected resin will penetrate and render it impervious.

## 3.8 Coefficient of Thermal Expansion

Graphite has a low coefficient of thermal expansion, which reduces the effect of thermal stresses in this material. (See Table 2.)

# 4 DESIGN

## 4.1 Existing Codes for Graphite Pressure Vessels

Currently there are no rules in the ASME Boiler and Pressure Vessel Code for the design and construction of graphite pressure vessels. Most of the recently constructed graphite pressure vessels follow the design and construction practices of the German pressure vessel code AD Merkblatt N2 [8], as well as experience driven procedures. These include requirements for materials, testing of graphite materials, marking, certification of quality, allowable stresses, tolerances and surface finish, and design calculations (including factors of safety for design and for pressure tests). Annex 3 to AD Merkblatt includes requirements for tension testing of graphite materials and the details of the tension test specimen. However, the acceptance criteria for mechanical properties to be used in design in AD Merkblatt N2 is less restrictive than that proposed for Part UIG.

The Dutch Rules for pressure vessels include Specification D 1401/83-12, Graphite Block Heat Exchangers [9], and M 0807/83-12, Impregnated Graphite [10], and reference AD Merkblatt N2 as part of the requirements for impregnated graphite.

## 4.2 Permissible Design Temperature

The German Technical Supervisory Board (Technische Uberwachungsverein, or TUV) permits a maximum design temperature of 200°C (392°F) for impregnated graphite vessels. AD Merkblatt N2 limits the minimum design temperature to -60°C (-76°F). The design temperature for impregnated graphite vessels to be designed and constructed to the proposed Part UIG is limited to the same values.

## 4.3 Properties for Design of Impregnated Graphite Vessels and Components

Pressure vessels and pressure components of impregnated graphite shall at least meet the requirements listed in Table 1.

## 4.4 Design Margins

In the mid-1970s, Union Carbide performed a series of tests to confirm the validity of the design margin of 5 on tensile strength that had been used for impregnated graphite since the 1930s (see section 3.2). Some additional testing has also been performed to confirm again the validity of the design margin of 5. Although this design margin has proved to be adequate, a design margin of 6 is proposed for part UIG.

## 4.5 Buckling of Cylindrical Shells

According to the German Pressure Vessel Code AD-Merkblatt N2 [8], paragraph 8.4, elastic buckling from external pressure need not be considered in the design. Because of low design stresses (compared to those for ferrous and nonferrous materials) and low D/t ratios, elastic buckling of graphite shells is not of concern. However, calculations need to be performed for plastic deformation, in which case the tensile strength value K used in the design is increased by a factor of 2.5 in Equation 4, which takes into account the higher compressive strength of impervious graphite compared to the tensile strength. In design of tubes under external pressure, the tensile strength value K may be increased by a factor of 2.

The allowable external pressure for plastic deformation in AD-Merkblatt B6 is given by the following equation:

$$p = 20\frac{K}{S}\frac{(S_e - C_1 - C_2)}{D_a}[Term], \text{ bar}$$

**Equation 4 - Allowable External Pressure for Plastic Deformation**

and

$$[Term] = \frac{1}{1 + \dfrac{1.5u\left(1 - 0.2\dfrac{D_a}{l}\right)D_a}{100(S_e - C_1 - C_2)}}$$

where

The factor 20 in Equation 4 includes a factor of 10 for conversion of MPa to bar

K/S = allowable compressive stress (= 2.5 times the allowable tensile stress, $S_t$), MPa

$S_e$ = nominal wall thickness, t, mm

$D_a$ = nominal outside diameter of cylindrical shell (D), mm

l = length of the cylinder between effective reinforcements (unstiffened length)

u = $2\left(\dfrac{D_{i\max} - D_{i\min}}{D_{i\max} + D_{i\min}}\right)100$, out-of-roundness, %

$D_i$ = inside diameter of cylindrical shell

$C_1$ = underthickness tolerance, mm ($C_1$ = 0 for graphite vessels)

$C_2$ = corrosion allowance, mm ($C_1$ = 0 for graphite vessels)

**Equation 5 - Allowable External Pressure for Plastic Deformation Term**

For small out-of-roundness values ($u < 0.5\%$), the equation for allowable external pressure reduces to the following:

$$P = 5\frac{S_t}{D}$$

**Equation 6 - Simplified Allowable External Pressure for Plastic Deformation**

This is a valid assumption because cylindrical graphite vessel components are machined from solid blocks and the machining tolerances can be considered as being much less than 0.5%. Under this assumption, the [Term] will always be greater than 0.9 and can be neglected (see Table 3).

**Table 4 - Value of [Term] for Various Tube and Cylinder Parameters**

| | $D_a$ | $s_e$ | u | l | [Term] |
|---|---|---|---|---|---|
| Tube | 2 | 0.25 | 0.5 | 2 | 0.9542 |
| | 2 | 0.25 | 0.5 | 40 | 0.9439 |
| | 2 | 0.25 | 0.5 | 120 | 0.9436 |
| | 2 | 0.25 | 0.5 | 400 | 0.9434 |
| Cylinder | 24 | 2 | 0.5 | 24 | 0.9328 |
| | 24 | 2 | 0.5 | 60 | 0.9235 |
| | 24 | 2 | 0.5 | 400 | 0.9183 |
| | 24 | 2 | 0.3 | 400 | 0.9494 |

## 4.6 Buckling of Tubes

The maximum allowable load on tubes shall be the lesser of the following:

$$F_B = \frac{EI\pi^2}{L^2(FS)}$$

where

$F_B$ = maximum allowable load on the tube to avoid buckling, lb (N)

E = modulus of elasticity of the tube, psi (N/mm$^2$)

I = $\frac{\pi}{64}\left(D_o^4 - D_i^4\right)$, moment of inertia of the tube, in$^4$ (mm$^4$)

L = maximum unsupported length of the tube, in (mm)

FS = design margin (FS = 6 for tubes in other than lethal service; FS = 7 for tubes in lethal service)

**Equation 7 - Allowable Load on Tubes, Buckling**

$$F_C = \frac{S_c A}{FS}$$

where

$F_C$ = maximum allowable load on the tube, lb (N)

$S_c$ = compressive strength of the tube material, psi (N/mm$^2$)

A = $\frac{\pi}{4}\left(D_o^2 - D_i^2\right)$, area of the tube, in$^2$ (mm$^2$)

$D_o$ = outside diameter of the tube, in$^2$ (mm$^2$)

$D_i$ = inside diameter of the tube, in$^2$ (mm$^2$)

FS = design margin (FS = 6 for tubes in other than lethal service; FS = 7 for tubes in lethal service)

**Equation 8 - Allowable Load on Tubes, Compressive**

## 4.7 Thicknesses of Flat Heads, Covers, and Tubesheets

The same formulas as in ASME Section VIII, Division 1 are used to calculate the thickness of flat heads and covers. The following formula is used for calculating the minimum thickness of flat heads and covers that are integral with the cylindrical shell:

$$t = d\sqrt{0.2\frac{P}{S_t}}$$

**Equation 9 - Minimum Thickness of Flat Heads and Covers**

The minimum thickness of a graphite flat head or cover that is gasketed to a cylindrical shell and held in place by a bolted steel backing plate is:

$$t = G\sqrt{0.3\frac{P}{S_t}}$$

where

t = thickness, in. (mm)

$S_t$ = allowable tensile stress, psi (MPa)

P = design pressure , psi (MPa)

d = nominal inside diameter, in. (mm)

G = the diameter at the location of the gasket load reaction, as defined in Section VIII, Division 1.

**Equation 10 - Minimum Thickness of Graphite Flat Head or Cover**

The minimum thickness of impervious graphite tubesheets is based on the TEMA formula RCB-7.132 for bending. This formula is not material specific, and is based on Timoshenko's thin plate theory. Because impervious graphite is a material that follows Hooke's law, this formula is applicable for calculating tubesheet thickness.

For fixed and floating tubesheets the minimum thickness shall be calculated using the following formula:

$$t = \frac{FG}{3}\sqrt{\frac{P}{\mu S_t}}$$

where

μ = ligament efficiency for bending, in accordance with UHX-11.4

F = 1.00 for fixed tubesheets

F = 1.25 for floating tubesheets

**Equation 11 - Minimum Thickness of Fixed and Floating Tubesheets**

For fixed tubesheets the pressure shall be based on the shell side or tubeside pressure, whichever governs, corrected for vacuum, if present, on the other side.

For floating tubesheets, the effective design pressure shall be calculated by use of Equation 12. The value obtained from Equation 12shall be used in Equation 11 to determine the minimum thickness of the tubesheet.

$$P = P_t + P_s \left[ \frac{1.25\left(D^2 - D_c^2\right)\left(D - D_c\right)}{DF^2 G^2} \right]$$

where

$P_t$ = tube side design pressure, psi (MPa) (for vacuum design, $P_t$ is negative)

$P_S$ = shell side design pressure, psi (MPa) (for vacuum design, $P_S$ is negative)

D = outside diameter of the floating tubesheet, inches (mm)

F = 1

$D_c$ = $\sqrt{\frac{4A}{\pi}}$, equivalent diameter of the tube center limit perimeter, C, inches (mm)

A = the total area enclosed by the tube center limit perimeter, C, where C is the length of the heavy line in the Figure 10 shown below.

**Equation 12 - Design Pressure of Floating Tubesheets**

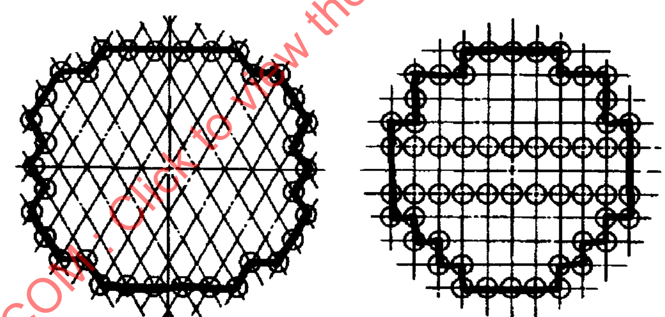


**Figure 10 - Tube Center Limit Perimeter**
(From TEMA RCB-7.132 [13])

## 5 NOZZLES

Permissible nozzle details are shown in Figure 9. The nozzle reinforcement shall be in accordance with Section VIII, Division 1 requirements, as far as they are applicable to graphite vessels. The minimum nozzle neck thickness is 1/2 in. (13 mm) for nozzles of 3 in. (75 mm) and greater and 1/4 in. (6 mm) for nozzles less than 3 in. (75 mm) nominal inside diameter.

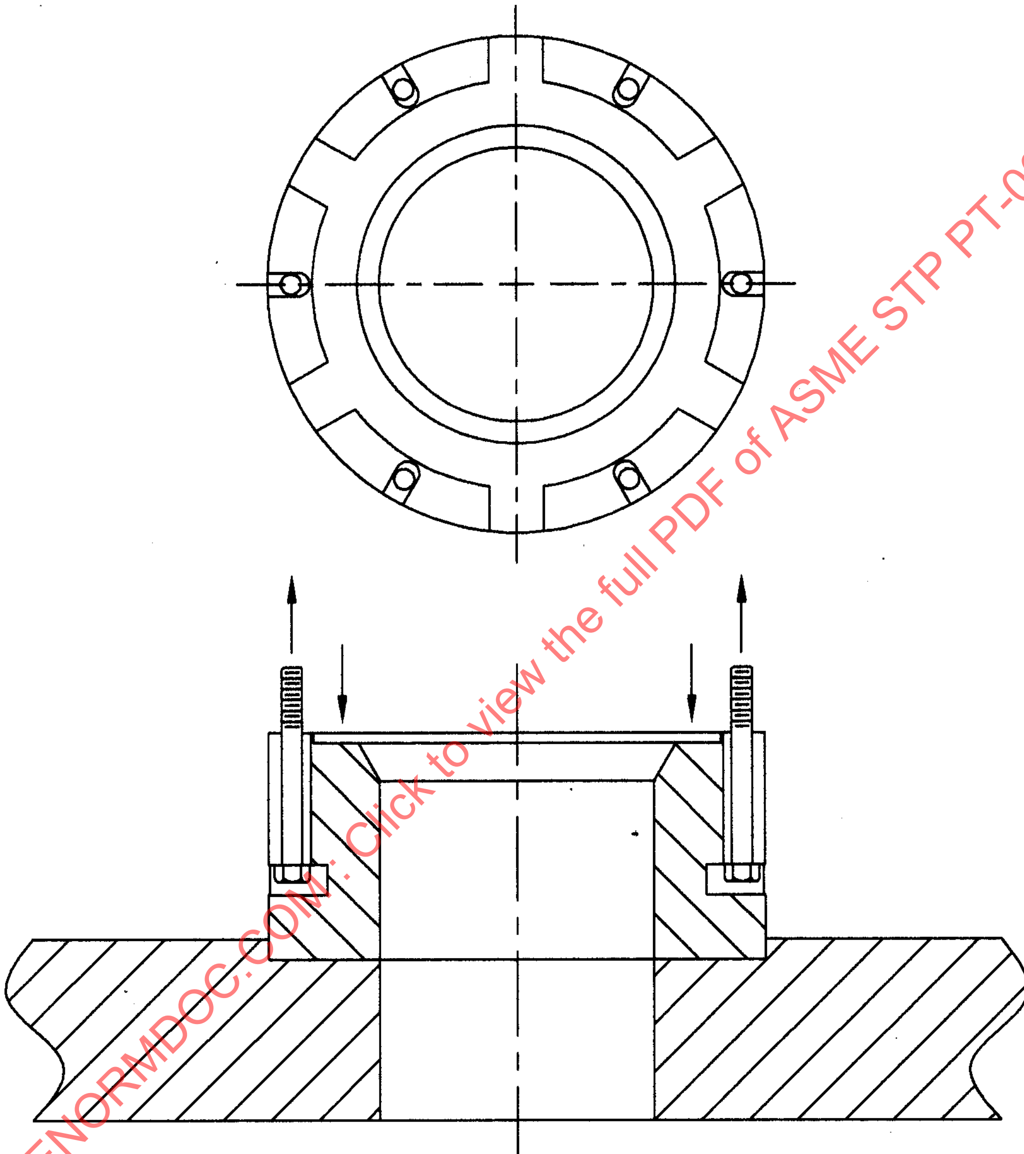


**Figure 11 - Acceptable Nozzle Details in Graphite Vessels, Example A**

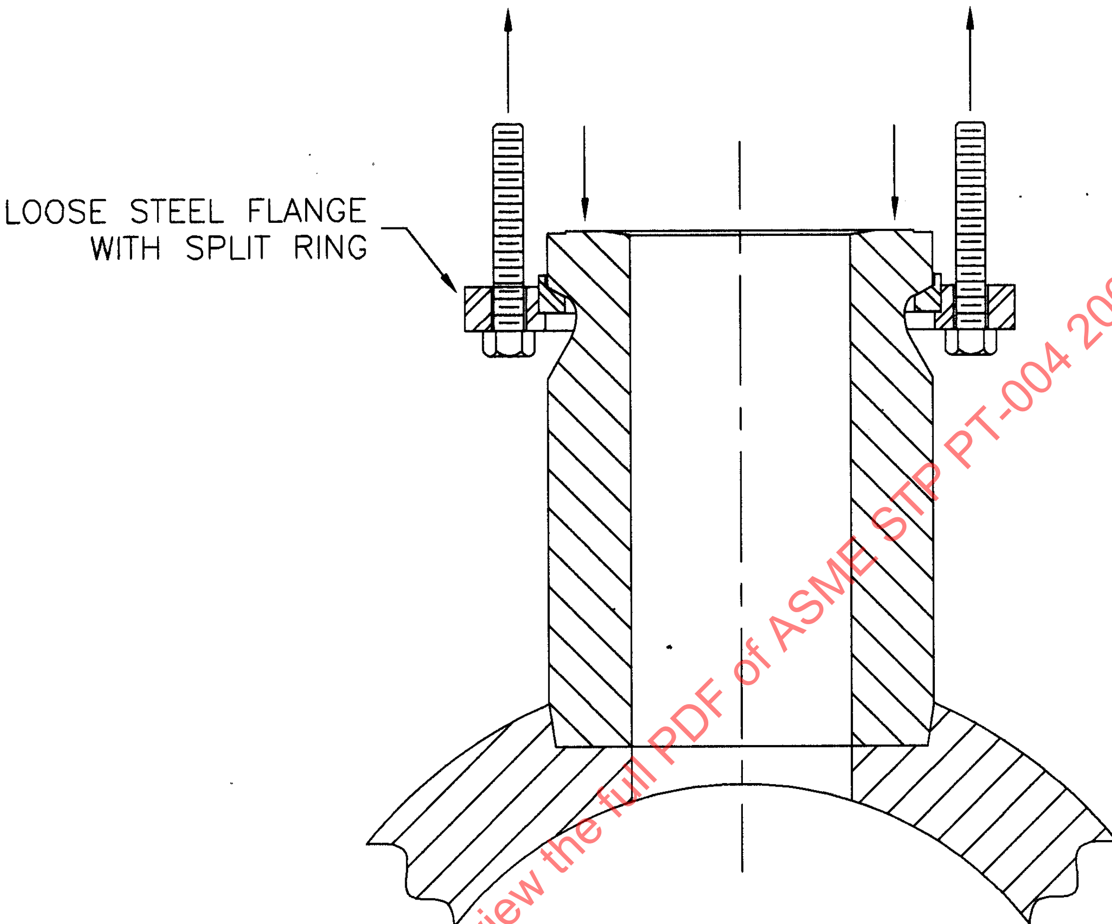



**Figure 12 - Acceptable Nozzle Details in Graphite Vessels, Example B**

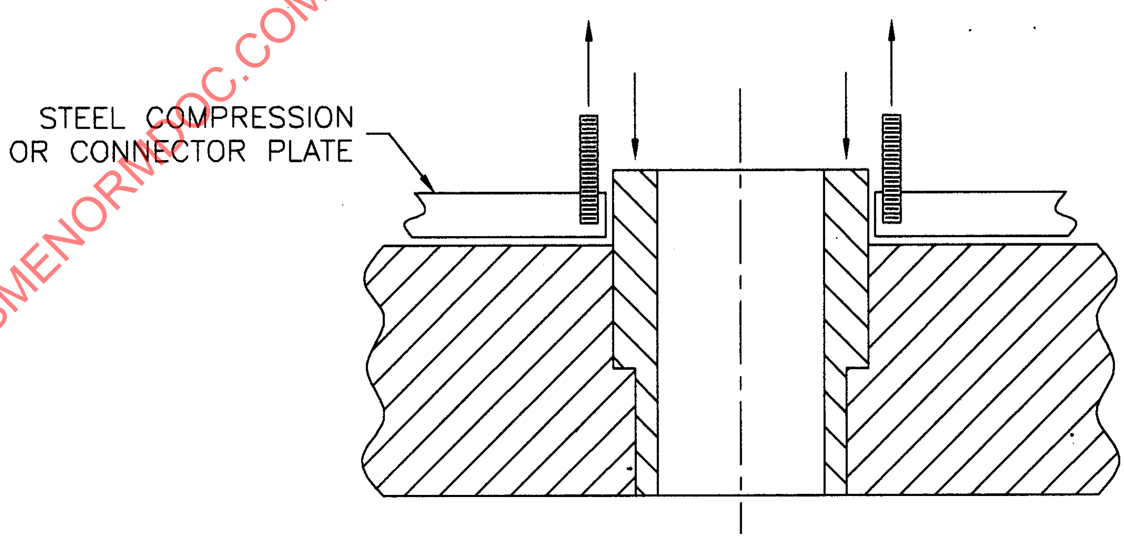



**Figure 13 - Acceptable Nozzle Details in Graphite Vessels, Example C**

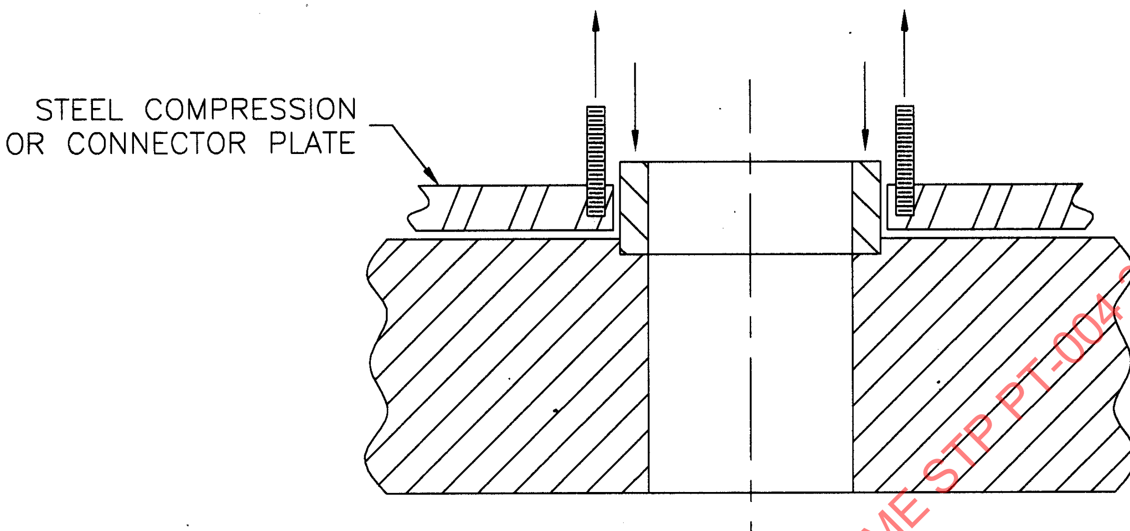
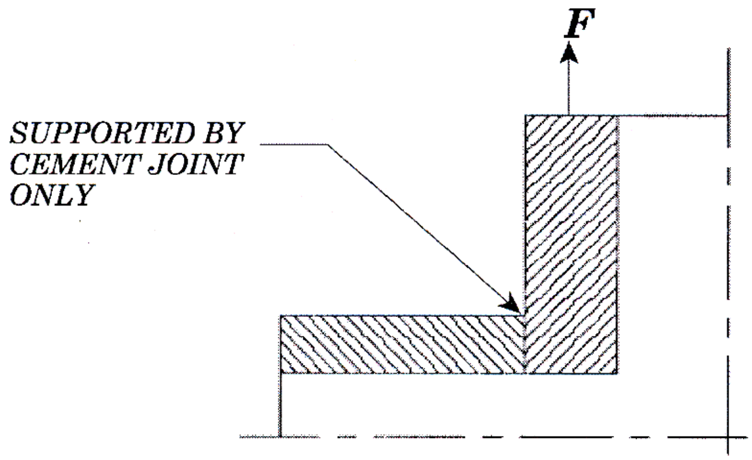
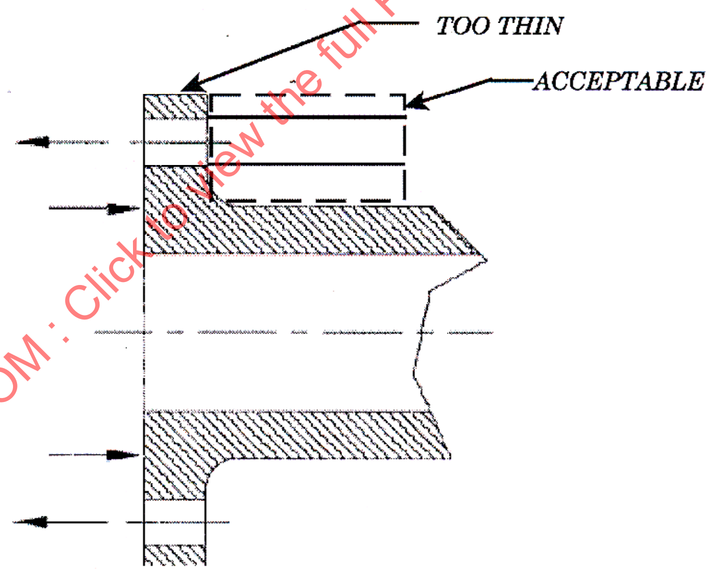



**Figure 14 - Acceptable Nozzle Details in Graphite Vessels, Example D**




(a) Corner Joint




(b) Graphite Flanged Nozzle

**Figure 15 - Unacceptable Nozzle Details**

Care must be taken to minimize loads on nozzles in graphite vessels and components. Flexible connections should be used for all connections to graphite components.

## 6 LETHAL SERVICE

Graphite vessels in lethal service are subject to the following additional requirements:

*(a)* The design margin shall be 7 for lethal service.

*(b)* In addition to the testing requirements in Table 4, all graphite components, excluding tubes, shall be designated a lot and shall be tested to determine mechanical properties (see Table 4). Tubes are already subject to proof testing (see section 9.2).

*(c)* All interior corners of pressure components shall have 1/2 in. (13 mm) minimum radius.

*(d)* Exposed graphite shall be shrouded to increase containment of product.

*(e)* Leak/permeability testing by monitoring of process fluids is highly recommended.

## 7 CERTIFIED MATERIAL SPECIFICATIONS

There are no American Society for Testing and Materials (ASTM) or ASME material specifications for impregnated graphite. The vessel parts are produced to a manufacturer's Certified Material Specifications (CMS). A CMS is a Certificate Holder's document that is developed when qualifying the material. The CMS shall include requirements for the raw materials and processes necessary to manufacture certified materials. The CMS shall include all essential and nonessential variables with specified tolerance ranges. The Manufacturer shall qualify the CMS using Certified Material Qualification (CMQ) forms.

### 7.1 Qualification of Certified Materials

A minimum of 10 specimens per test are required to qualify the manufacturer's CMS. This sample size is based on the assumption that the material properties are randomly distributed about the mean. A manufacturer's review of tensile strength data for a 1-year period showed the assumption to be valid.

The t-distribution is a symmetrical, bell-shaped distribution with a mean of zero and a standard deviation of 1. As the number of samples increase, the t-distribution approaches the normal distribution. The t-distribution is used when the sample size is small ($n < 30$), and the population standard deviation is unknown. The t-distribution shall be used to predict the mean value of the mechanical properties (tensile strength) for the material being qualified.

A confidence interval can be developed for the population mean $\mu$, such that

$$\frac{X-\mu}{P\left(t_{\frac{\alpha}{2}} \le \frac{S}{\sqrt{n}} \le t_{\frac{\alpha}{2}}\right)} = 1-\alpha$$

where

P = probability function

n = sample size (number of samples)

$t_{\frac{\alpha}{2}}$ = the value of the t-distribution that defines a boundary yielding an area A under one side of the symmetric distribution

X = sample mean

$\mu$ = population mean

S = standard deviation about the sample mean

$1 - \alpha$ = confidence interval

**Equation 13 - Confidence Interval**

The preceding equation can be reduced to

$$\mu = X + t_{\frac{\alpha}{2}} \frac{S}{\sqrt{n}}$$

**Equation 14 - Simplified Confidence Interval**

Thus an interval can be established with a specified confidence level (95%) in which the mean value of the tensile strength is located. However, the proposed Part UIG requires all specimens to be within ±20% of the sample mean which forces the interval in which μ is located to be considerably smaller. As the interval for μ becomes smaller, the upper and lower limits of μ approach the X ± 20% values. Thus the t-distribution provides the assurance, to a 95% confidence level, that the population mean is within the established interval. The X ± 20% values make the interval smaller.

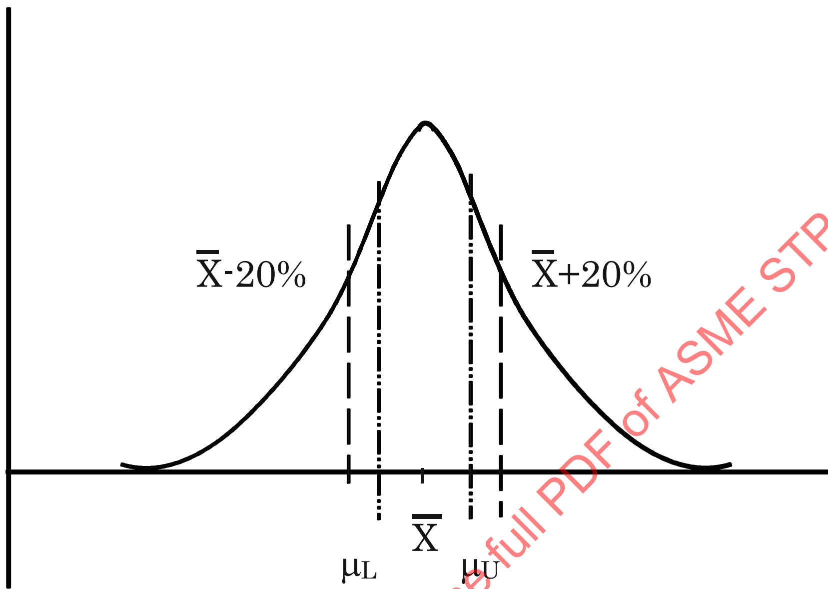



**Figure 16 - t-Distribution of Material Test Data**



The X ± 20% test values force the manufacturer to control the variability of the manufacturing process by requiring uniform test specimens. For example:

**Table 5 - Hypothetical Test Data (1000 psi)**

| Process 1 (Out of Control) | Process 2 (In Control) |
|---|---|
| 2 | 2.8 |
| 5 | 3.5 |
| 4 | 3.2 |
| 2 | 2.9 |
| 3 | 3.0 |
| 1 | 2.6 |
| 3 | 3.0 |
| 4 | 3.6 |

| Process 1 (Out of Control) | Process 2 (In Control) |
|---|---|
| 2 | 2.7 |
| 6 | 3.1 |

Process 1

X = 3.2 S = 1.549, $\mu_L$ = 2.032, $\mu_u$ = 4.368

X - 20% = 2.56, and X + 20% = 3.84

Process 2

X = 3.04, S = 0.324, $\mu_L$ = 2.81, $\mu_u$ = 3.27

X - 20% = 2.43, X + 20% = 3.65

For process 1, all but two tensile strength values are outside of the X ± 20% limits, which indicates the manufacturer's process is out of control; therefore, the material can not be qualified.

For process 2, all tensile strength values are inside of the X ± 20% limits; therefore, the manufacturer is controlling the process, and the material can be qualified. Note the allowable stress is

$$S_a = \frac{X - 20\%}{6} = \frac{0.8X}{6}$$

**Equation 15 - Allowable Stress**

For lethal service,

$$S_a = \frac{X - 20\%}{7} = \frac{0.8X}{7}$$

**Equation 16 - Allowable Stress, Lethal Service**

The manufacturer is required to test every 3 months five samples of the material being produced to assure the mechanical properties are within acceptable limits. The proposed Part UIG will require the strength values to be within 20% of the average value determined during material qualification testing. The only purpose in testing five material specimens is to provide assurance the mechanical properties have remained the same over time. Increasing the sample size to 10, or 15, or 20 would not appreciably increase the assurance the material properties have remained constant because all test values must be within the specified limits.

## 8 CERTIFIED CEMENT SPECIFICATIONS

The Manufacturer shall prepare a Certified Cement Specification (CCS) using the Certified Cement Qualification (CCQ) form. A CCS is a Certificate Holder's document that is developed when qualifying the cementing material. It includes the raw materials and the process necessary to manufacture certified cement. It includes all the essential and nonessential variables with permissible tolerance ranges. Any change to any essential variable requires requalification of the CCS.

The following are the essential variables to be included in the qualification of a CCS:

*(a)* Materials, including:

*(1)* composition

*(2)* filler

*(3)* resin

*(4)* accelerator

*(b)* Curing process (time, temperature, etc.)

Nonessential variables are those elements which the manufacturer may include in the CCS to provide direction in producing certified cement, but which do not affect the resulting properties of the material. Changes to nonessential variables do not require requalification of the CCS. The CCS shall include the results of tension tests.

### 8.1 Cementing Procedure Specification

The Manufacturer shall prepare a Cementing Procedure Specification (CPS) using the Cementing Procedure Qualification (CPQ) form. The CPS is a certificate holder's document that is developed when qualifying the cementing procedure. The CPS shall include the materials and procedures necessary to manufacture items using certified material and certified cement. The CPS shall include all essential and nonessential variables with the permissible tolerance ranges. Any change to any essential variable shall require requalification of the CPS. The Certified Cementing Procedure Specification (CPS) shall include the results of tension tests.

The following essential variables shall be included in the qualification of a CPS:

*(a)* Joint design

*(b)* Certified Cement Specification

*(c)* Surface preparation

*(d)* Curing time and temperature range

*(e)* The design clearance used in qualification.

# 9 TESTING OF GRAPHITE MATERIALS

Certified materials shall be subjected to the type of tests and test frequency as specified in Table 4. Figure 17 through Figure 20 show the details of the test specimen used for tension testing of graphite block material and graphite tubes. The proposed Part UIG will include the following standard test methods for testing graphite materials as appendices to that document:

*(a)* *Appendix I.* Standard Test Method for Determining the Flexural Strength of Certified Materials Using Four-Point Loading

*(b)* *Appendix II.* Standard Test Method for Determining the Flexural Strength of Certified Materials Using Three-Point Loading

*(c)* *Appendix III.* Standard Test Method for Determining the Tensile Strength of Certified Carbon and Graphite Materials

*(d)* *Appendix IV.* Standard Test Method for Compressive Strength of Carbon and Graphite

*(e)* *Appendix V.* Testing the Coefficient of Permeability of Carbon and Graphite

*(f)* *Appendix VI.* Thermal Expansion Test Method for Graphite and Impregnated Graphite

## 9.1 Block Material

The following are some of the testing requirements for block material:

*(a)* The strength of certified block material shall be established by the tensile strength test defined in Appendix II and the compressive strength defined in Appendix III.

*(b)* The test specimens shall be as specified in Appendix II and Appendix III.

*(c)* The tensile strength and compressive strength for each lot of material shall be within 20% of the average value determined during the certified material qualification tests.

## 9.2 Tube Material

The following are some of the testing requirements for tube material:

*(a)* The tensile strength of certified tube material shall be established by the tensile strength test defined in Appendix III.

*(b)* The strength values for each lot of material shall be within 20% of the average value determined during the certified material qualification tests.

*(c)* After impregnation all extruded heat exchanger tubes shall be subjected to an internal hydrostatic test or a pneumatic test (to be performed under a protective cover) at a minimum of 290 psi (2 MPa) or two times the design pressure, whichever is greater. The results shall be documented by the tube manufacturer.

**Table 6 - Testing Requirements for Certified Materials**

| Property | Testing Frequency |
|---|---|
| Flexural strength | (1) Tubes: Each lot,[a] every 3 months, minimum (except for graphite blocks). |
| Compressive strength | (1) Tubes: At the time of certified material qualification, thereafter calculated property based upon a specific relationship with flexural strength tests.<br>(2) Blocks: Each lot, every 3 months, minimum. |
| Tensile strength at room temperature | (1) Tubes: At the time of certified material qualification, thereafter calculated property based upon specific relationship with flexural strength tests.<br>(2) Blocks: Each lot, every 3 months, minimum. |
| Tensile strength at maximum material design temperature | At the time of certified material qualification for tubes, blocks, and cement. |
| Cement tensile strength | Only certified cement manufacturing process may be used. Based upon this certification, the tensile strength test shall be performed at the time of certified material qualification. |
| Coefficient of thermal expansion | The value shall be determined by tests performed at the time of certified material qualification. |
| Coefficient of permeability | The value shall be determined by tests performed at the time of certified material qualification. |

[a]A lot is that quantity of certified material made from the same raw materials, the same chemical control mix, and the same manufacturing process produced within the tolerances of the essential variables of the impregnation process in conjunction with a 3-month testing program.

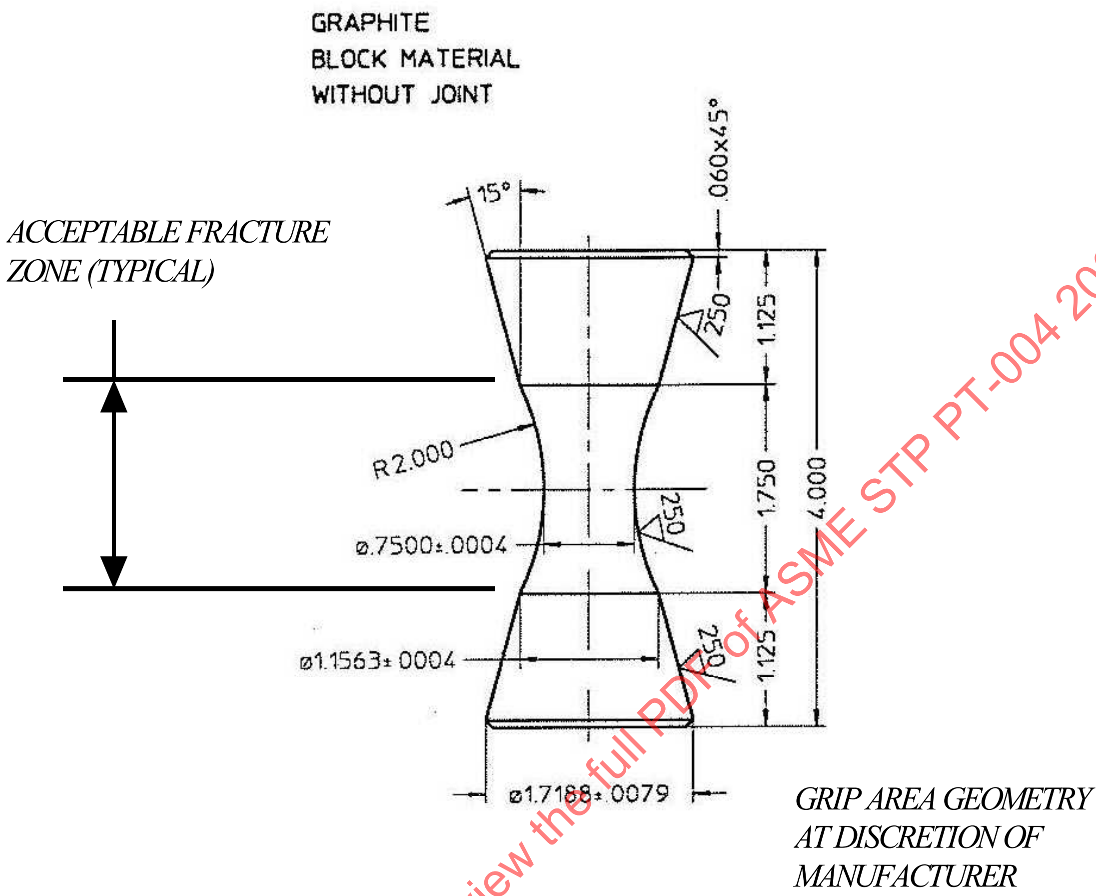



**Figure 17 - Tensile Test Specimen**
(from SGL Drawing SK4322-01)

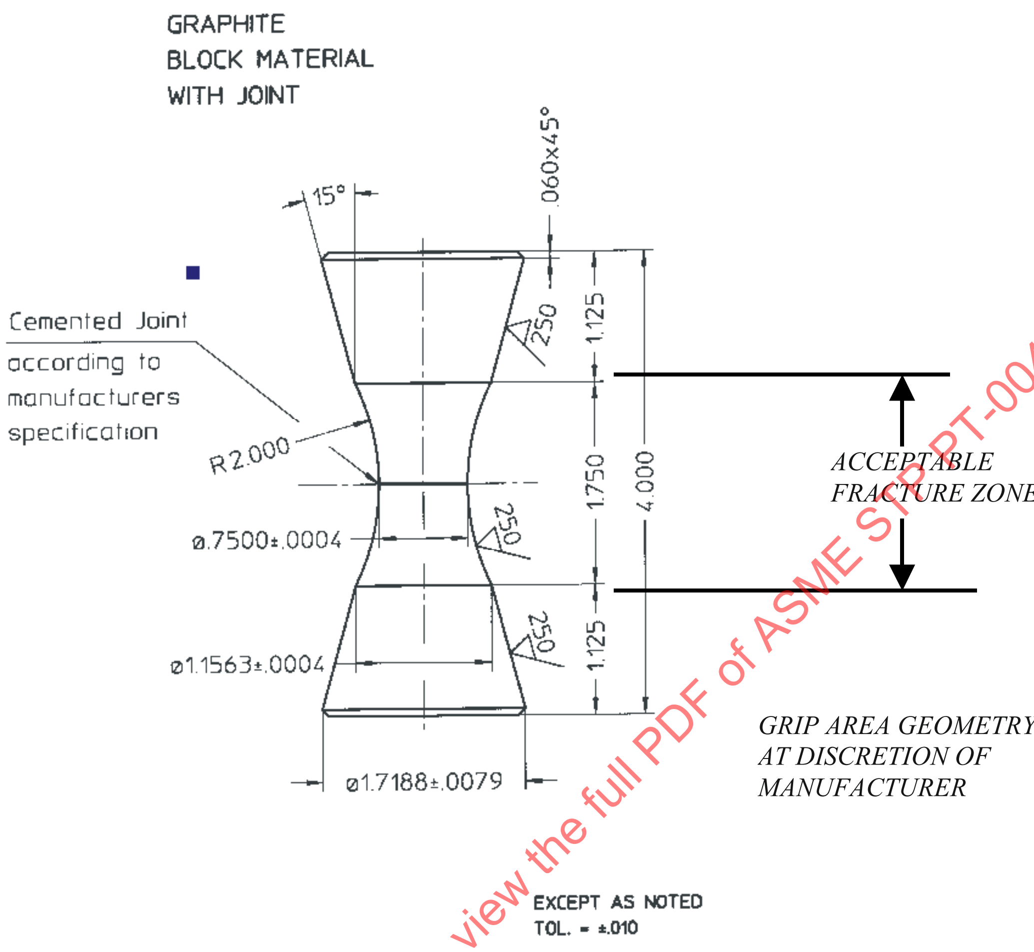



**Figure 18 - Cement Material Tensile Test Specimen**
(from SGL Drawing SK4322-02)