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IMPREGNATED GRAPHITE FOR PRESSURE VESSELS

ASME STANDARDS TECHNOLOGY, LLC

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IMPREGNATED GRAPHITE FOR PRESSURE VESSELS

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The Special Working Group on Graphite Pressure Equipment

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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.