

Final Report
Project No. B-153

FUSED SILICA MANUAL

by J. D. Fleming

Associate Project Director

J. W. Johnson

Group Leaders

Paul Boland

S. H. Bomar

Prepared for

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FOREWORD

This document constitutes the final report under U. S. Atomic Energy Commission Contract No. AT-(40-1)-2483, sponsored by the Fuels and Materials Development Branch, Mr. J. M. Simmons, Chief, of the Division of Reactor Development, and administered by the Oak Ridge Operations Office Reactor Division, Dr. David F. Cope, Director. The contract covered the period from November 14, 1958, to July 1, 1964.

This contract was performed in the High Temperature Materials Branch, Mr. J. D. Walton, Head, of the Georgia Tech Engineering Experiment Station, Chemical Sciences and Materials Division, Dr. Frederick Bellinger, Chief. The project was directed by Dr. J. D. Fleming. Mr. J. W. Johnson served as Associate Project Director.

In addition to the work described in this report, an investigation was made under Contract No. AT-(40-1)-2483, of reaction kinetics in Al-U₃O₈ dispersions. This research is reported in a separate document.

CHAPTER I

INTRODUCTION

- § 1.1 Scope
- § 1.2 Method of Approach
- § 1.3 Nomenclature
- § 1.4 General Comparison of Commercial Forms
- § 1.5 References for Chapter I

§ 1.1 Scope

The applications of fused silica may be divided into four arbitrary categories, each of which emphasizes a different combination of properties:

a. Laboratory Applications

The chemical inertness and resistance to thermal shock of fused silica make it ideally suited to the construction of laboratory apparatus and to use as premium glassware. This was one of the earliest uses of fused silica and continues as one of the most widespread.

b. Optical Applications

Unique transmission characteristics and a very low coefficient of thermal expansion qualify fused silica as an ideal material for critical lens, lightguide, window, and mirror applications.

c. Electrical and Electronic Applications

The high specific resistance and dielectric strength of fused silica promote its use as insulation in many types of critical equipment. The stability of these characteristics with temperature, a favorable dielectric constant and loss tangent, good high temperature strength, and excellent thermal shock resistance are bringing increased attention to fused silica for use in constructing radomes for reentry and hypersonic vehicles.

d. Structural Applications

Since fused silica is refractory, has good high temperature strength, corrosion resistance and insulating capacity, and an unexcelled resistance to thermal shock, it should be widely applicable as a refractory structural material. This should be particularly true in nuclear facilities in which the additional properties of low neutron absorption cross section and resistance to radiation damage would be most attractive.

These categories are not mutually exclusive. Many applications are evident in which more than one set of properties are important, such as use as a window in orbital vehicles. Here, the optical clarity, strength, thermal shock resistance, and radiation damage resistance combine to suit fused silica to use as a structural unit which also functions as an optical component. Although these categories are not firmly restrictive, they do serve to illustrate emphasis on particular properties with secondary advantages to be drawn from other properties.

While the first three categories have been brought to a rather high stage of development, application of fused silica as a structural material has been grossly neglected in the United States and has not reached its full potential in the United Kingdom, the European countries, or Russia. This lack of broad application as a structural material is largely due to the high cost of fused silica when fabricated by even the most modern glass-working techniques. This objectionable characteristic of fused silica has now been substantially reduced by the application of powder metallurgy techniques, principally slip-casting, to the fabrication of very large and complex shapes. This method of fabrication has resulted in a radical decrease in the cost of structural grade fused silica ^{1/}, bringing it into economic competition with other materials suitable for use in the same temperature range. In addition, the unique combination of properties which characterizes fused silica may, in many cases, permit simplified design which would be prohibited by other more conventional materials. In such a case, the overall cost of construction with slip-cast or glass-worked fused silica may well be lower than that with any

^{1/}See § 1.4.

other material.

This report represents an attempt to gather in one source the data which will be required to evaluate fused silica for a particular structural application. The major emphasis is placed on data representing the mechanical behavior and environmental response of fused silica with only limited reference to optical and electrical characteristics.

§ 1.2 Method of Approach

In keeping with the intended use of this report and to avoid undue length, the data are summarized with a minimum of critical scientific comment. As with any engineering data book, the reader should regard the data as representative of the class of material only. If a particular property is of crucial importance, the original literature should be consulted and the manufacturer of the specific material to be purchased should be contacted. Every effort has been made to exclude invalid data, however, and the data included are felt suitable for design use.

In spite of the current trend in research toward use of the cgs system of units, most design work is now, and probably will continue to be, in the British system. Since this report is intended principally for engineering use, units are employed which are familiar to engineers. In most cases, these are British units. Conversion factors and a temperature conversion table appear inside the front and back covers of the report.

Presentation of the data is in graphical form, wherever possible, to facilitate engineering use. This results in sacrifice of several significant figures in some cases and the original reference should be consulted if greater accuracy is desired.

Almost all the data for slip-cast fused silica were drawn from reports under this contract which covered an extensive experimental program during the period from November 14, 1958, to July 1, 1964. The additional data were located from a survey of the manufacturers listed in Chapter XI and a search of the following abstracts:

<u>ASTIA 1/</u>	1925-1963
<u>British Ceramic Abstracts</u>	1925-1963
<u>Ceramic Abstracts</u>	1925-1963
<u>Chemical Abstracts</u>	1925-1963
<u>Nuclear Science Abstracts</u>	1947-1963
<u>Scientific and Technical Aerospace Reports</u>	1951-1963
<u>U. S. Government Reports</u>	1951-1963

§ 1.3 Nomenclature

Considerable confusion has arisen in the literature as to proper appellation of fused silica products. While all such products are nominally pure vitrified silicon dioxide, they will show more or less significantly different properties as a result of the type of raw material and process used in their manufacture. Perhaps the most common, but by no means universal, commercial nomenclature is:

Fused Quartz: Transparent 'vitreous' silica produced from clear crystalline quartz.

Fused Silica: Vitreous silica produced from sand. May be transparent, translucent, or opaque depending on the concentration of small gas bubbles entrapped during fusion.

Pressed Fused Silica: Porous vitreous fused silica formed by hot pressing vitrified silica prepared from sand. Not yet a commercial product.

Quartz Glass: Same as fused quartz. Sometimes synonym for transparent fused silica.

Silica Glass: Same as fused silica.

1/Machine Search.

Sintered Fused Silica: Vitreous silica prepared by powder metallurgy techniques, including slip-casting and pressing.

Slip-Cast Fused Silica: Porous vitreous silica formed by sintering a casting formed in a plaster mold from an aqueous suspension of vitrified silica prepared from sand.

Synthetic Fused Silica: Highly pure vitreous silica produced from silica resulting from conversion of a silicon compound. Most often produced by hydrolysis of silicon tetrachloride, a volatile compound which can be purified by distillation.

Vitreous Quartz: Same as fused quartz.

Vitreous Silica: Same as fused silica.

In this report, fused silica is used as the generic term for vitreous silica products. In the description of specific data, the designations of fused quartz, transparent fused silica, translucent fused silica, slip-cast fused silica, pressed fused silica, and synthetic fused silica are used as defined above. In many cases, a sharp distinction is not made in the literature between transparent fused silica and fused quartz. For most structural use, the two may be considered identical.

§ 1.4 General Comparison of Commercial Forms

The principal differences among the various commercial forms of fused silica, from the standpoint of structural design, are in cost and porosity.

The cost of fused silica products varies greatly. As a very rough indication of the price ranges, Table I lists the approximate cost of the commercially available forms with the exception of synthetic fused silica which is used only in non-structural applications.

TABLE I
ROUGH COSTS OF COMMERCIAL FUSED SILICA*

<u>Form</u>	<u>Bulk, Not Shaped</u> (\$/lb.)	<u>Simple Shapes</u> (\$/lb.)
Transparent, Optical Grade	40	80
Transparent, Utility Grade	16	30
Translucent	5	10
Slip-Cast	0.5	1.5

*Very approximate. May vary by factor of two or more.

The cost difference among the various forms is seen to be quite large. In considering these comparisons with regard to structural applications, one additional point should be made. With increasing complexity of shape, the costs of the glass-worked products will rise extremely rapidly while that of slip-cast fused silica will increase little if at all. In addition, fabrication of a large number of identical pieces by glass-working techniques will decrease the cost per unit by perhaps 10 per cent but the decrease in unit cost with slip-casting will be as much as 60 per cent.

The high cost of fused silica produced by glass-working techniques is easily understandable from the properties of the molten material. Below 3000° F, fused silica is entirely too viscous to be worked and even at 3200° F the melt is about the consistency of "cold tar" (5). The lower limit for practical working, set by the viscosity, is approximately 3300° F (2). In this temperature range, the vapor pressure of fused silica is quite high and working above 4500° F is difficult. At this temperature, 40 per cent of a normal working shape will volatilize in five minutes (2). In the normal working temperature range, the mechanical problems resulting from the very viscous melt are compounded by the difficulty of obtaining materials of construction for the fabrication system which can withstand both the temperature and chemical attack by the molten silica (1).

The problems associated with glass-working of fused silica preclude production of high surface area shapes with gas blow torches and the fused silica industry did not reach its full growth until development of resistance heated furnaces (4) and mold forming apparatus heated by induction (7). The remarkable fact about glass-worked fused silica is not that it failed to reach widespread industrial use rapidly but that its properties were exceptional enough to result in development of a fused silica industry at all (6). Even with the staggering problems associated with glass-working fused silica, commercial interest was such that fused silica flasks of 200 gallon capacity and 21-inch diameter pipes were being produced commercially by 1927 (3).

For structural applications, the cost of transparent fused silica is usually prohibitive in spite of the fact that its mechanical properties are superior to those of the other forms. Unless optical clarity is required, the translucent and slip-cast forms will usually be selected as a result of their much lower cost. These are normally considered to be the structural forms of fused silica. The design properties of the two structural forms are much the same.

The major point to be considered in selecting one of the two structural forms of fused silica is whether the structural application involves gas or liquid containment. If not, there will seldom be any reason to select the more expensive, impermeable translucent fused silica over the normally permeable slip-cast fused silica. If containment is a problem, the possibility of sealing the surface of slip-cast fused silica should be considered 1/. Even with such surface treatment, slip-cast fused silica is likely to be much less expensive than the glass-worked form.

The only other situation, which is likely to be encountered with any frequency, in which translucent fused silica would be preferable to the slip-cast form is an application involving sliding friction. It is possible, although no studies have been made, that the translucent form would have a greater wear resistance.

1/See § 3.18.

§ 1.5 References for Chapter I

1. Besborodov, M. A., "Manufacturing Quartz Glass, Its Properties and Applications," Keram. i Steklo 10 3 (1934).
2. DeMaria, Vincent C., "Fused Quartz Fabrication," Presented at the Seventh Symposium on the Art of Glassblowing. The American Scientific Glassblowers Society (1962).
3. Hutton, R. S., "Development of the Fused Quartz Industry," Trans. Am. Electro-Chem. Soc. 51 (preprint) 5 (1927).
4. Kershaw, J. B. C., "Quartz Glass and Silica Ware," Industrial Chemist 1 208 (1925).
5. Marconnay, A. von Beaulieu and T. Frantz, "Fused (opaque) Quartz, A German Construction Material," Chem. Fabrik 9 27:299 (1936).
6. Pincus, A. G., "Glass From the Atomic View," Ceram. Age 39 [No. 2] 38 (1942).
7. Quartz Et Silice, Brit. 283, 174, Feb. 29, 1928.

CHAPTER II

THE STRUCTURE OF FUSED SILICA

- § 2.1 Introduction
- § 2.2 Oxides of Silicon
- § 2.3 Phases of Silica
- § 2.4 Sluggish Transformations in Silica
- § 2.5 Rapid Transformations in Silica
- § 2.6 Chemical Bonding in Fused Silica
- § 2.7 Molecular Structure of Fused Silica
- § 2.8 Theories of the Structure of Fused Silica
- § 2.9 Residue Structure in Fused Silica
- § 2.10 Demonstration of Short Range Order
- § 2.11 Temperature Variations of Short Range Order
- § 2.12 Non-Stoichiometry
- § 2.13 Water Content
- § 2.14 Summary
- § 2.15 References for Chapter II

§ 2.1 Introduction

As will be seen in this chapter, fused silica is an extremely complex material on the atomic scale. As opposed to most substances, it is characterized by great variability and there is some doubt that there is any "true" fused silica structure.

While a complete discussion of the nature of fused silica is far beyond the scope of this treatment, some appreciation of the problems involved is essential to the engineer dealing with fused silica as a structural material. A basic knowledge in this area is helpful in understanding the differences among various samples of fused silica, the need for careful control of processing variables, and the limitations governing use in service.

For a more detailed treatment of the material in the following sections, the monumental treatise of Sosman (36) should be consulted.

§ 2.2 Oxides of Silicon

There are two known oxides of silicon, the monoxide (SiO) and the

dioxide, silica (SiO_2). While some doubts have been expressed as to the existence of silicon monoxide as a distinct species, it is at least uniform enough to be classified according to distinct properties (11, 48).

Silicon monoxide is used as a separate compound in a few applications such as the formation of amorphous substrates for electron microscopy where its low density and electron transparency combine to advantage with its uniformity and lack of surface features as an evaporated film. Its only importance in a consideration of fused silica stems from its occasional presence as an impurity, particularly when the silica is melted in an electric furnace with graphite electrodes. In structural applications, the presence of silicon monoxide in the usual amounts is unimportant. Excessive quantities of silicon monoxide may cause foaming of fused silica at high temperatures.

§ 2.3 Phases of Silica

Silica occurs in approximately two dozen different modifications (20, 34, 40, 41, 42). Of these, the most commonly encountered forms are fused silica, quartz, cristobalite, and tridymite (9). Fused silica is amorphous on a macroscopic scale and is formed by reasonably rapid cooling of melts of any of the crystalline forms. Quartz is a hexagonal crystalline form, found in nature as sand and rock crystal, and is the source of all commercial fused silica with the exception of synthetic fused silica. Cristobalite is a tetragonal crystalline form which is the usual product of the crystallization, or devitrification, of fused silica at elevated temperatures. Tridymite is an orthorhombic crystalline form sometimes found as a byproduct in the production of silica glass. There is some controversy as to whether tridymite is a distinct phase of silica, with some investigators maintaining that it is a true stable phase (16) and others concluding that it is a binary unstable phase (18, 19).

§ 2.4 Sluggish Transformations in Silica

Transformations among the crystal forms of silica occur at extremely low rates. In order to produce a given phase from another, it is frequently necessary to maintain the temperature within the region of greatest stability of the desired phase for several days before the conversion

approaches completion. The very slow rate of these reactions renders their experimental study quite difficult and often leads to erroneous conclusions (37).

Of more importance in a consideration of the properties of fused silica is the fact that the melting of quartz or cristobalite is also very sluggish. Quartz transforms very slowly to cristobalite beginning at about 1600° F (38), and cristobalite is then, for all practical purposes, stable to its melting point of about 3110° F (39). Since the conversion of quartz to cristobalite is quite sluggish, however, it is possible to heat quartz to 2660° F, without formation of significant amounts of cristobalite, where it melts to form fused silica (29). Since fused silica does not show a point of sharp viscosity change with temperature 1/, it has no true melting point.

The melting of quartz or cristobalite proceeds so slowly that retention of some crystalline material in a commercial fabrication process is difficult to avoid. Quartz fuses from the surface of the grains inward at rates of 4.5×10^{-2} and 7.7 microns per minute at 2860° and 3160° F respectively (2). Assuming a constant rate and neglecting the formation of cristobalite, about 25 minutes would be required to fuse 200 micron particles of sand at 3160° F. This is approximately the sand particle size and temperature used in commercial electric fusion furnaces. In view of the relatively poor heat transfer characteristics of a packed sand mass, it is evidently difficult to achieve complete fusion. In practice, the unmelted quartz will often convert to cristobalite and further cristobalite will form during cooling of the fused silica. As a result, commercial fused silica often contains a small amount of cristobalite which is detectable by x-ray diffraction. In addition, as discussed below, the best fused silica retains some characteristics of the crystalline silica from which it is prepared.

§ 2.5 Rapid Transformations in Silica

In addition to the slow conversions of one crystal form to another mentioned above, the silica phases commonly show transformations from one polymorph to another within the same crystal form. Such changes involve structural reorientation of the atoms only and do not involve the breaking

1/See § 4.10.

and reformation of Si-O bonds. As a result, these polymorphic inversions are much more rapid, reaching completion in less than 0.125 second during the inversion of the β high temperature form of cristobalite to the α low temperature form (47).

Not suprisingly, in view of the sluggishness of their interconversion rates, the various crystal forms of silica show a tendency to exist in an imperfectly ordered state. In consequence, the temperature at which a polymorphic inversion occurs varies, depending on the source and thermal history of the material.

Since cristobalite is the usual product of devitrification of fused silica, its inversion is the only one of interest with regard to structural applications of fused silica. Depending on its source, cristobalite undergoes the α - β inversion from approximately 340° F when highly disordered to approximately 510° F when highly ordered (6, 17, 49). The inversion also shows some degree of hysteresis so that the density does not return to its original value when the cristobalite is heated through the inversion and cooled (14, 23, 24).

The densities of quartz and cristobalite, calculated from the x-ray data of Johnson (22), are compared with that of fused silica in Figure 1.

§ 2.6 Chemical Bonding in Fused Silica

In the crystalline forms of silica, the basic structural unit is the silica tetrahedron, a group consisting of a silicon atom surrounded by four oxygen atoms at positions forming a tetrahedron (9). Zachariasen pointed out that this structural unit must also be present in fused silica since any different oxygen distribution would produce an energy potential high enough to make ordering and crystallization inevitable during cooling of molten silica (54). Since Zachariasen's original suggestion, the tetrahedral oxygen distribution has been experimentally proved by several different techniques. The tetrahedral arrangement in cristobalite, quartz, tridymite, and fused silica is clearly seen, for example, from infrared spectra (1).

The nature of the chemical bond in the silica tetrahedron can be demonstrated by an electron density map derived from careful analysis of

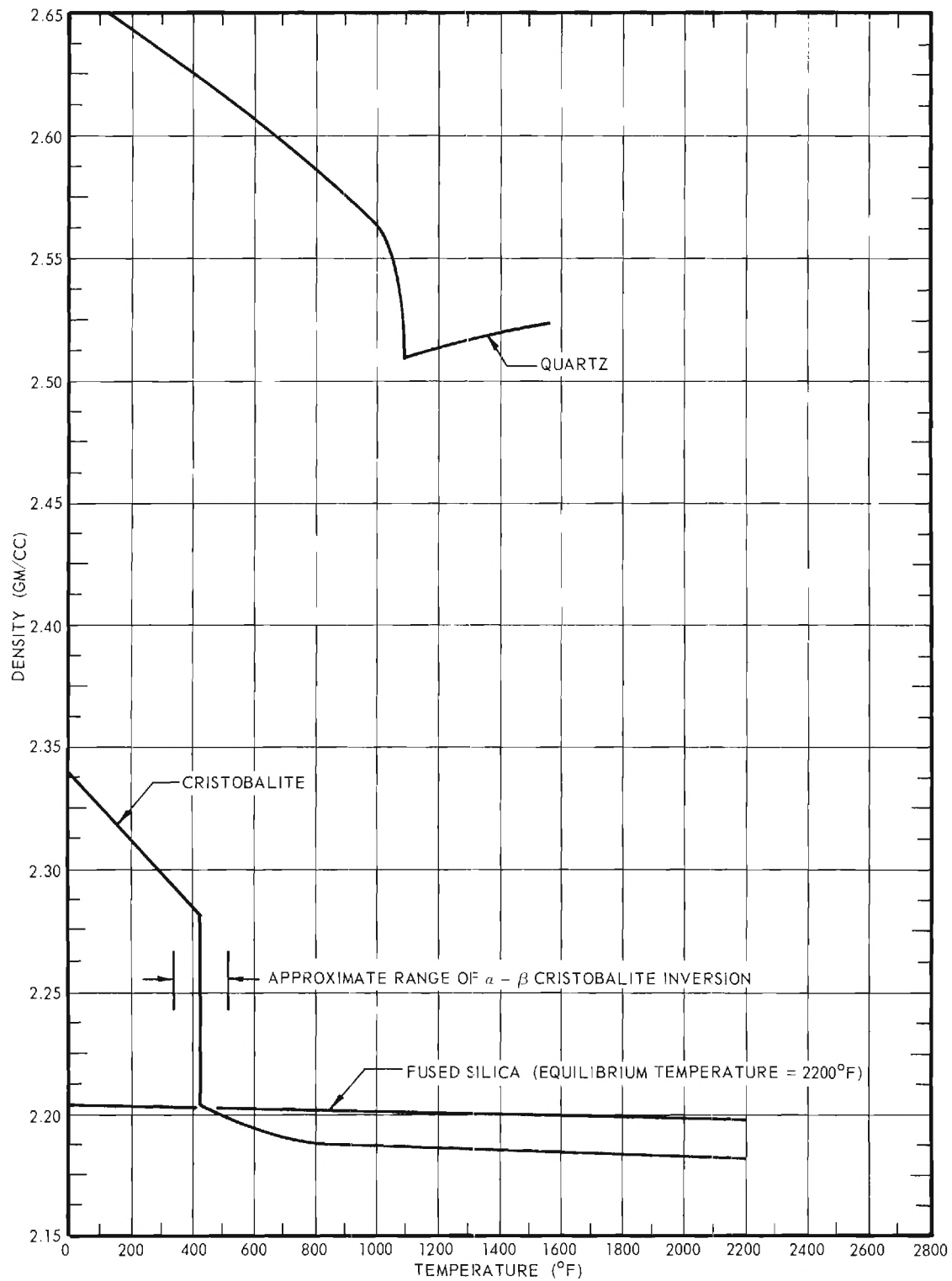


Figure 1. Densities of Quartz, Cristobalite, and Fused Silica Compared.

x-ray diffraction patterns. While this technique has not been applied to fused silica, well defined maps have been developed for some of the crystalline forms of silica. Although the bond angles and distances will certainly be distorted in fused silica, nevertheless the nature of the chemical bond should not be qualitatively different and the results of the electron density maps for the crystalline forms should also be representative of fused silica. An electron density map for quartz shows high density regions between silicon and the four nearest oxygen atoms, characteristic of ionic bonding (8). In the regions between adjoining tetrahedra, however, the electron density is diffuse while true ionic bonding would produce large charge-free areas. The electron density map thus shows the chemical bonding in silica to be mixed ionic and covalent, perhaps with a leaning toward covalency. Zarzycki has determined the average values of the configuration parameters of silica tetrahedra in fused silica (55). The Si-O distance is $1.60 \pm 0.05\text{\AA}$ and the Si-Si distance is $3.00 \pm 0.05\text{\AA}$. The Si-O-Si angle is $143 \pm 17^\circ$.

§ 2.7 Molecular Structure of Fused Silica

In the crystalline forms of fused silica, the tetrahedra are joined by shared tetrahedral oxygen atoms. The arrangement of the tetrahedra can follow several different geometries, each of which is characteristic of that particular form of silica. In any given form, the tetrahedra show a regular three dimensional orientation which extends for great distances, giving rise to the characteristic crystal lattice representative of the form (9). X-ray diffraction patterns of the crystalline forms of silica consequently show distinct reflection lines which characterize the particular crystal lattices. X-ray diffraction patterns of fused silica, however, show only a broad amorphous hump with no distinct reflection peaks. This indicates that the molecular structure of fused silica is completely disordered within the limits of resolution of ordinary diffraction techniques. As a result, fused silica is described as being amorphous.

In spite of the disordered structure shown by conventional x-ray diffraction, more refined techniques capable of higher resolution show anomolous behavior which does not confirm the existence of complete

disorder (53). Instead, the results imply that very small regions of order, approximately 10 to 100 Å in extent, exist within the macroscopically disordered structure. The concept of fused silica as a completely random structure must then be altered to a model consisting of small local regions which are ordered but which show no regular orientation with respect to each other. If attention is focused on a particular tetrahedron, this model suggests that the first few surrounding tetrahedra are regularly oriented with respect to the reference tetrahedron. Moving further out, the orientation becomes increasingly irregular with respect to the reference until an indefinite boundary is crossed, past which the orientation becomes more regular again as a second reference tetrahedron is approached. The two reference tetrahedra, however, are not oriented with respect to each other. Fused silica is thus more accurately described as a material which displays short range order but no long range order. A simple, though obviously not accurate, analogy might be drawn to a polycrystalline metal in which the grain size corresponds to only a few unit cells and the grains are joined with a preponderance of distorted grain boundary material.

Active controversy has been raging for more than thirty years over an accurate analysis of the structure of fused silica. A full discussion of the various approaches to this problem is completely beyond the scope of this report. Further discussion will be limited to a brief description of the more simple theories of the structure of fused silica and a summary of the recent work which indicates short range order in fused silica.

Two invaluable translations of Russian literature are available which treat the theoretical and experimental approaches to the structure of glassy materials (43, 44). These texts afford an excellent review of the data available and the discussions in the first (43) demonstrate with clarity the turbulence of the continuing controversy over the proper description of the structure of glass.

§ 2.8 Theories of the Structure of Fused Silica

Zachariasen proposed the Random Network Theory to describe fused silica (54). In this model, the short range order extends no further than the two tetrahedra which share a common oxygen atom. The next series of tetrahedra

are pictured as being substantially disoriented with respect to this origin oxygen atom although all tetrahedra are joined through shared oxygen atoms into a continuous random skeleton network. This model shows no more than six oxygen-second oxygen closest approaches and accounts for ordered regions approximately 8 \AA in extent.

A second model of glass structure is proposed by the Crystallite Theory which was formalized by Lebedev (25). This model pictures glass as consisting of microcrystals "in the form of islets joined by interlayers with a distorted transitional structure". The extent of short range order in this model is somewhat greater than that pictured by Zachariasen, perhaps at least 30 \AA .

The third model for the structure of fused silica is exemplified by the Vitron Theory of Tilton (45). This model pictures fused silica as consisting of characteristic structural units, called vitrons, which are so highly distorted that they cannot extend far enough to show long range order. Tilton's model consists of silica tetrahedra arranged through shared oxygen atoms in pentagonal rings which, in turn, form common interfaces between dodecahedral cages. Since this type of symmetry is inconsistent with the long range order required for crystal formation, the dodecahedral structure can propagate in three dimensions only to a limited extent and would necessarily be strained and distorted. Each of these limited network clusters of tetrahedra is called a vitron. The vitrons are pictured as being held together by a relatively distorted and weakened structure consisting of occasional shared pentagonal rings and oxygen bridges.

Tilton's construction of the vitron was apparently guided by the early estimates of the Si-O-Si bond angle as about 180° in fused silica and β -cristobalite. Mackenzie has pointed out that more accurate measurements have shown the bond angle to be between 142 and 155° for α - and β - quartz, α - and β -cristobalite, and fused silica (27). This evidence controverts Tilton's vitron model but the concept of such a structural unit of different configuration is not disproved and the general theory still has merit.

As pointed out by many investigators, the various structural theories differ more in degree than in kind, although there are important fundamental differences.

§ 2.9 Residue Structure in Fused Silica

An important contribution to the understanding of the structure of fused silica has recently been made by Mackenzie (28). Since the fusion rates of quartz and cristobalite are quite low 1/, complete elimination of crystalline material during melting requires scrupulous care. Essentially any commercial fused silica may thus be expected to contain residual crystalline material. In most cases, since fused silica is usually produced from quartz, this residue will be quartz but, since quartz can convert to cristobalite 1/, residual cristobalite may well occur. This residue will be distributed throughout the fused silica and, in addition, cristobalite may form, principally on exposed surfaces 2/, by devitrification of the fused silica during cooling or subsequent treatment.

Mackenzie studied the characteristics of this retained material in fused quartz and fused cristobalite using x-ray diffraction, electron metallography, infrared absorption, and hardness measurement. Retained crystalline material of the order of about 0.1 micron size was demonstrated in quartz fused for 30 minutes at 3380° F. In quartz fused at higher temperatures, distinct crystalline residue was no longer detected although some indications of its presence were still noted. It is apparent, of course, that such residue may be of any crystal size and that the residue structure in well-fused silica may easily be fine enough to make differences in the residue structure and short range order indistinguishable. The short range order and residue structure may well be merely different aspects of the same problem.

The probability of a crystalline residue must be kept in mind when evaluating experiments designed to demonstrate short range order in fused silica such as those in the following sections. Presence of a residue too fine to be detected by microscopy or x-ray diffraction will still give results which could be misinterpreted as showing short range order intrinsic in the fused silica itself. Unfortunately, the experiments infrequently include

1/See § 2.4

2/See § 6.3

an evaluation of the extent of residue structure in the specimens employed and conclusions concerning supposed short range order must be accepted with reserve. This problem is obviously acute since melting of any form of silica can yield a micro-crystalline structure which may be any of the crystalline forms of silica, as a result of the possibility of their interconversion, and which may either have formed from truly molten silica or been retained from incomplete melting.

§ 2.10 Demonstration of Short Range Order

a. By X-ray Diffraction

Calculations of the electronic distribution curves for vitreous silica from x-ray diffraction studies indicate that the structure is not completely disordered. Oberlies and Dietzel (30) concluded from such studies that fused silica shows a prevalence of structural units consisting of six silica tetrahedra organized in a ring. Some rings are open or incomplete and the tetrahedra appeared to be distorted. X-ray traces at 500° F and 2370° F indicated a structure much like that of β -cristobalite, but more open and distorted.

Using the same approach, Zarzycki (55) found no indication of a cristobalite-like structure. He concluded that the Si-O-Si bond angle stability up to 2900° F indicated a residual α -quartz structure.

b. Neutron diffraction

Breen carried out studies, similar to those using x-ray diffraction, by examining the differential scattering of neutrons by fused silica (4). He found better resolution than is obtainable with x-rays and concluded that fused silica shows six oxygen-second oxygen closest approaches. In contrast to most other studies, this indicates a short range order extending only through about two silica tetrahedra, as pictured by Zachariasen's model 1/.

1/See § 2.8.

c. Irradiation Defects

Weeks and Nelson studied the generation of defects in irradiated silica (50). The defect structure was examined by electron-spin-resonance. They concluded that short-range order similar to α -quartz exists over a region greater than 5 \AA .

d. By Optical Absorption

Richter, et al, investigated the interference intensity of fused silica (33). They concluded that the cristobalite structure persists over approximately 25 \AA regions.

Winter-Klein found that the infrared absorption curve of fused silica showed discontinuities at temperatures corresponding to the inversion points of the various crystalline forms of silica (52). The existence of very small crystallites of all the crystalline forms was postulated. Somewhat similar conclusions were reached by Florinskaya and Pechenkina (13).

e. By Electron Microscopy and Diffraction

Shishacov concluded from a study of electron diffraction that crystallites of about 20 \AA size were present in fused silica powder (35). Considerable doubt was cast on the validity of this conclusion by Lukesh who pointed out that the method of sample preparation used was likely to cause surface devitrification (26).

Oberlies detected quartz, cristobalite, and tridymite in fused silica but implied that this was due to crystalline residue (31).

Zarzycki and Mezard carried out a series of most interesting studies using transmission electron microscopy (56). The specimens were produced within the microscope column, minimizing the effects of atmosphere contamination. They were able to demonstrate a distorted microcrystallinity of approximately $50\text{-}100 \text{ \AA}$ extent.

f. By the Moessbauer Effect

Pollak, et al, carried out a study of the Moessbauer effect in fused quartz (32). A large fraction of the diffused iron nuclei omitted without recoil, indicating crystalline behavior in small regions.

g. By Low Temperature Specific Heat

Dank and Barber analyzed the low temperature specific heat of fused silica and concluded that the structure must be anisotropic (7). The order required to produce this anisotropy was determined to be somewhat in excess of that implied by Zachariasen's theory.

h. By γ -Radiation Discoloration

Fischer irradiated quartz rock crystal and fused silica using a Co-60 source (12). He found that the rock quartz crystal was uniformly discolored while most fused silica samples showed only patches of discoloration. This patchy discoloration was proved to result from a residue structure rather than from centers of short range order by subsequent examination of samples treated to produce a lower order of retained crystallinity.

i. By Hardness Testing

Westbrook studied the variation of hardness with temperature for fused quartz, fused cristobalite, and synthetic fused silica (51). The fused quartz and synthetic fused silica showed discontinuities in the hardness-temperature curve at approximately the α - β inversion temperature of cristobalite. Westbrook interpreted his results as possible support for Tilton's vitron model 1/ but recognized the possibility of a residue structure in his sample.

§ 2.11 Temperature Variations of Short Range Order

Even if the short range order in fused silica is no different from the order noted in liquids near their freezing points, this order can be expected to have some influence on the physical properties of the material. Tool has pointed out that a liquid in equilibrium at a given temperature is described by a characteristic energy distribution, reflected by definite relationships between its molecules (46). During equilibration following a change in

1/See § 2.8.

temperature, the energy distribution shifts to a new characteristic peak and the molecular relationships rearrange accordingly. Tool noted that the sluggish transformations and high viscosity typical of silica indicate a low molecular mobility so that the changes in energy distribution require some time to become complete. As a result, moderately rapid cooling or heating is likely to prevent complete readjustment of this distribution so that the final molecular arrangement is representative of some temperature between the temperature at which the cooling or heating started and that at which it terminated. A fictitious equilibrium temperature, sometimes called the fictive temperature, is defined as the temperature at which the equilibrium energy distribution is the same as the energy distribution of the specimen as it exists. Rapid heating or cooling yields an equilibrium temperature approaching the temperature at which the heating or cooling started while a slower rate of temperature change produces an equilibrium temperature closer to the terminal temperature.

The effects of varying the equilibrium temperature are easily detected and demonstrate the validity of the concept. Douglas and Isard found that the thermal expansion coefficient of slowly heated fused silica over the temperature range 1800 - 2700° F was negative as opposed to the positive coefficient of rapidly heated fused silica (10). This was confirmed by Brückner who also found that the thermal expansion coefficient in rapidly heated fused silica varied with the equilibrium temperature (5) 1/. The equilibrium temperature also affects the viscosity of fused silica 2/. On equilibration at a constant temperature, following prolonged exposure to a higher temperature, the viscosity decreased by an order of magnitude in one specimen examined by Isard and Douglas (21).

§ 2.12 Non-Stoichiometry

As it is usually prepared, commercial fused silica is in a reduced state. This is equivalent to saying that it contains some silicon monoxide 3/.

1/See § 4.8

2/See § 4.10

3/See § 2.2

The silica chain is broken at the point of reduction by removal of tetrahedral oxygen and triple coordination is substituted for the normal quadruple coordination of oxygen at that point (3).

The departure from stoichiometry can be demonstrated by oxidation, both from the resulting weight gain and from the pronounced increase in ultra-violet transmission which accompanies the return of quadruple coordination (3).

The effects of non-stoichiometry on physical properties are not known. The only effect which has been proved is a decreased devitrification tendency 1/.

§ 2.13 Water Content

Water vapor tends to dissolve in fused silica and to diffuse uniformly throughout the structure. The diffusing species is probably the hydroxyl radical since the water molecule can react with a shared tetrahedral oxygen atom to produce two hydroxyl radicals and fission of the silica network at that point.

Since the silica network is broken at points of hydroxylation, the physical properties would be expected to show corresponding alterations and such alterations are observed. In addition to marked decreases in infrared transmission, an increased water content decreases the viscosity and density and increases the thermal expansion coefficient (15).

§ 2.14 Summary

A summary of the various aspects of the fused silica structure appears useful at this point. The structure is governed by:

- a. Short range order involving small regions of regularity over about 10-100 Å.
- b. Residue consisting of small crystallites of the parent material, usually quartz, remaining after fusion.

1/See § 6.5

- c. Liquid structure, which may be indistinguishable from the short range order, determined by the equilibrium temperature.
- d. Nonstoichiometry resulting from generation of triply coordinated silicon atoms by reduction.
- e. Chain scission caused by formation of hydroxyl groups from dissolved water.

Each of these contributing effects to the silica structure shows some influence on physical properties, though limited in many cases, and each is dependent to a degree on the manufacturing process and source material. Fused silica may thus be expected to vary to some extent from specimen to specimen. In reality, it would appear most difficult to form two exactly identical specimens as a result of the multiplicity of factors which must be controlled.

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CHAPTER III

FABRICATION

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- § 3.2 Fabrication by Glass Working
- § 3.3 Fabrication by Pressing
- § 3.4 Fabrication by Slip-Casting
- § 3.5 Production of the Master Pattern
- § 3.6 Selection of Plaster for the Working Mold
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§ 3.1 Introduction

Fused silica may be fabricated by glass-working and by powder metallurgy techniques. The glass-working techniques involve raising the temperature to the point that the silica viscosity becomes low enough to permit plastic deformation. The powder metallurgy techniques involve shaping the material at temperatures well below those used in the glass-working processes. Only two powder metallurgy processes have been explored to date, slip-casting and hot pressing.

Each of the three basic processes has characteristic advantages and disadvantages and none is suitable for all purposes. In general, the glass-working techniques yield materials of the highest density and are amenable

to the production of extremely complex shapes. These methods are the only commercial processes suitable for the production of optical parts. The glass-working methods suffer principally from high cost and the need for specialized equipment and skilled technicians for the production of any but the most simple shapes.

Hot pressing has not been fully developed as a commercial process and its comparison with slip-casting and glass-working is thus somewhat speculative. It appears that this method may offer advantages of dimensional control and speed in producing short-run shapes and yield a product of density intermediate between that obtainable by glass-working and by slip-casting. Estimation of the cost of hot pressing is not possible based on the work in the literature. It appears likely that, with further work, the cost can be brought below that of the glass-working techniques but it is doubtful that it will reach the level of slip-casting. The greatest disadvantages with hot pressing will probably be inability to handle shapes of much complexity and a requirement for specialized equipment.

The chief advantages of slip-casting are the lowest cost of all fabrication methods, ability to handle complex shapes, and a freedom from special equipment. Its principal disadvantage is that the densities obtainable are limited to approximately 86 per cent of theoretical.

As a result of the nature of the processes, few users of structural fused silica will fabricate shapes by either glass-working or hot pressing. In contrast, most users of slip-cast fused silica find it more convenient and less expensive to carry out the fabrication in their own plants. In this chapter, consequently, detailed attention will be given to slip-casting and only a very abbreviated mention will be made of glass-working and hot pressing.

§ 3.2 Fabrication by Glass Working

Classification of fused silica fabrication methods under the simple heading of glass-working is quite misleading in that it implies only a few closely related processes. Actually, there are many such processes which have been developed and these have little in common except that in all, the fused silica is worked in the plastic state at high temperatures, usually in the range from 3000 to 4500° F, most often at about 3600° F. At the risk of

considerable oversimplification, these methods can be grouped into a few more or less distinct categories.

The oldest method, and still widely used, of fabricating fused silica is by the use of a torch. Oxy-propane or oxy-hydrogen flames provide the most easily controlled conditions for such work. The high volatility of silica usually makes flame working difficult with hotter sources such as an oxy-acetylene torch or arc-plasma jet. The material is brought to the working temperature and shaped with the aid of graphite or molybdenum tools. Pieces may be joined by fusion together or, preferably, by shaping a v-notch in the pieces and welding with a fused silica rod.

Fairly simple shapes may be cast without a mold in a resistance or arc-furnace. The resistors or arc electrodes are submerged in sand, raised to temperature, and sand surrounding the rods is fused into a rough tube which is contained by the unmelted outer sand. In the case of arc melting, the arc is usually moved slowly down the length of the container to generate a more uniform fused mass.

Fused silica may be fabricated by glass molding. Resistance heating is normally used and the molten silica is often forced into the mold under pressure, vacuum, or centrifugal force. Blow-molding is also applied.

Pre-heated fused silica ingots may be shaped by rolling, pressing, or drawing. This method is most often applied to the fabrication of tubing, crucibles, beakers, and other small long-run parts.

Since such a cursory discussion has been given to the glass-working techniques, a review of the available literature is mandatory. Bottomley's review (5) is of great historical interest since the early stages of the development are presented through the eyes of an author who was himself instrumental in advancing fused silica. A similarly interesting historical review is presented by Stephenson (18). The recent review by Hetherington and Jack in Ullmanns Encyclopedia (13) presents an excellent coverage of the manufacture of fused silica and its fabrication by glass-working techniques as well as a summary of optical and physical data. A good discussion of torch working techniques is given by DeMarta (6) and Frost (9, 10). Espe's book on materials for high vacuum technology (7) includes

a good section on manufacture and fabrication of fused silica as well as a summary of physical properties and a comparison with other commercial glasses. Interesting information, particularly pictures of shapes which have been produced by glass-working techniques, is included in several recent reviews (1, 2, 11, 22).

§ 3.3 Fabrication by Pressing

Corning Glass Works has fabricated fused silica by means of its Multiform process (23). This is apparently not being done on a commercial scale and little information concerning the process is available. It presumably involves cold pressing silica with a binder followed by sintering at relatively high temperatures.

Vasilos has made a study of hot pressing of fused silica (19). Powders in three particle size ranges, $-295 + 208$ mesh, $-104 + 74$ mesh, and 5 micron average, were hot pressed at temperatures from 2000 to 2200° F, using pressures of 1000 and 2500 psi. At 2200° F and 1000 psi, the density of the compact reached approximately 87 per cent of theoretical in 10 minutes and approximately 99 per cent in 25 minutes. Little effect of particle size was noted.

Although the hot pressing process has not been applied on a commercial scale, Vasilos was able to produce fairly large shapes. A nose cone approximately six inches in diameter and 12 inches tall is illustrated in his article.

§ 3.4 Fabrication by Slip-Casting

Slip-casting of fused silica involves the following steps:

- a. Machining a positive master pattern having the same configuration as desired in the casting.
- b. Casting negative working molds from the master pattern using a commercial mold plaster.
- c. Coating the working mold with a release agent which permits easy removal of the casting.
- d. Filling the mold with silica slip, an aqueous suspension of fused silica.

- e. Allowing time for the porous plaster working mold to absorb water from the slip, leaving behind a solid casting of fused silica.
- f. Removing and drying the casting.
- g. Firing the casting.

The casting which results is a porous, opaque, white body with a smooth surface finish.

The slip-casting process is discussed in detail in the following sections 1/.

§ 3.5 Production of the Master Pattern

The master pattern may be made from any material which can be machined easily, is dimensionally stable, and does not absorb water from or react with the basic plaster slurry. The most commonly used materials are wood, usually mahogany which is lacquered after machining, brass, aluminum, lucite, or stainless steel. If only a few working molds are to be cast, one of the less expensive and more easily machined materials such as brass or aluminum should be used. If many working molds are to be prepared, the increased expense of a stainless steel pattern is well worth-while since such a pattern will be more resistant to corrosion and marring of the surface during handling.

The overall shrinkage from the master pattern to the fired casting will be approximately one per cent. If this tolerance is acceptable, the master pattern may be machined to the dimensions desired in the casting. If not, allowance may be made in design of the master mold or the casting may be machined after a bisque firing or final firing 2/.

The master pattern should be machined so as to facilitate casting of the working mold. This is discussed in a later section 3/.

No special precautions are necessary in design of the pattern other than avoidance of sharp corners, wherever possible, to minimize stress concentration in the casting in service. On long straight projections, a "draw" is desirable to facilitate removal of the casting from the mold. This

1/Information given without a citation was drawn generally from periodic reports under this contract. If the topic was discussed in a particular report, a citation is given. Consult Appendix B for a list of periodic reports.

2/See § 3.17.

3/See § 3.7.

consists merely of machining the projection with a slight taper in the direction in which the casting will be removed from the mold. If such a taper is undesirable, the mold is designed to separate along the axis of the projection to permit the casting to be removed.

§ 3.6 Selection of Plaster for the Working Mold

Experience with slip-casting fused silica has indicated that any good mold plaster will yield satisfactory results for most applications. Detailed studies were made of three types, U. S. Gypsum Pottery Plaster No. 1, U. S. Gypsum Puritan Plaster, and Bestwall No. K-59 Plaster (27).

Molds prepared from all three plasters at compositions ranging from 64 to 80 parts of water per 100 parts of plaster, by volume, produced castings whose fired strengths failed to show statistically significant differences. Although the Puritan plaster produced slightly higher casting rates and was slightly weaker than the other two, all three plasters seemed to have essentially the same handling qualities.

Samples cast in the three types of plaster were examined for surface contamination by x-ray fluorescence (31). In these tests, Keltex 1/ was used as a mold release and removed before fluorescence analysis. Additional samples were cast in Puritan plaster, some with Keltex and some with no mold release. These specimens were subjected to fluorescence analysis as removed from the mold. The results of these studies are summarized in Table II.

Table II indicates that calcium is the only impurity which shows any marked variation. The remaining impurities are probably from the slip itself. Contamination of the casting surface by calcium is not surprising since the acidity of the slip 2/ tends to leach the calcium from the mold. Since calcium is quite active in promoting devitrification 3/, the importance of a mold release is evident. The high surface calcium content in the sample tested with the Keltex in place compared with that in the same sample after removal of the Keltex indicates that calcium diffusion is restricted by the

1/See § 3.8.

2/See § 3.9.

3/See § 6.6.

TABLE II
SURFACE CONTAMINANTS IN SLIP-CAST SILICA

Plaster	Treatment	Fe (ppm)	Zr (ppm)	Mo (ppm)	Ca (ppm)
Bestwall K-59	Keltex removed before testing	29	22	18	10
Gypsum No. 1	Keltex removed before testing	38	30	25	11
Gypsum Puritan	Keltex removed before testing	27	17	29	3
Gypsum Puritan	Keltex in place during testing	24	17	28	38

Keltex film. The apparent difference between calcium pickup from Puritan and the other two plasters is probably attributable to differences in the manufacturing processes which render the Puritan less subject to acid leaching.

The effects of calcium pickup on surface devitrification were also evaluated. Samples cast under different conditions were subjected to continuous x-ray diffraction to determine the rates of cristobalite growth at 2200° F. These studies were made in air using a specially designed hot stage (32). The results are shown in Figure 2. In examining Figure 2, attention should be given to the fact that these curves represent the devitrification rate of the outer layer of the specimen only. This layer will devitrify much faster than the bulk of the specimen ¹/₁.

The surface devitrification rate of the specimen cast in Puritan plaster is lower than that of specimens cast in the other plasters, consistent with the variation in the surface calcium contents given in Table II. The mold release agents are seen to be effective in preventing calcium pickup since all the curves for samples cast with a mold release are somewhat lower in slope than those for castings produced without a mold release or fired with Keltex in place.

The danger in firing the casting without first removing the Keltex is also apparent from Figure 2. The sodium content of the Keltex itself and the calcium

¹/See § 6.3.

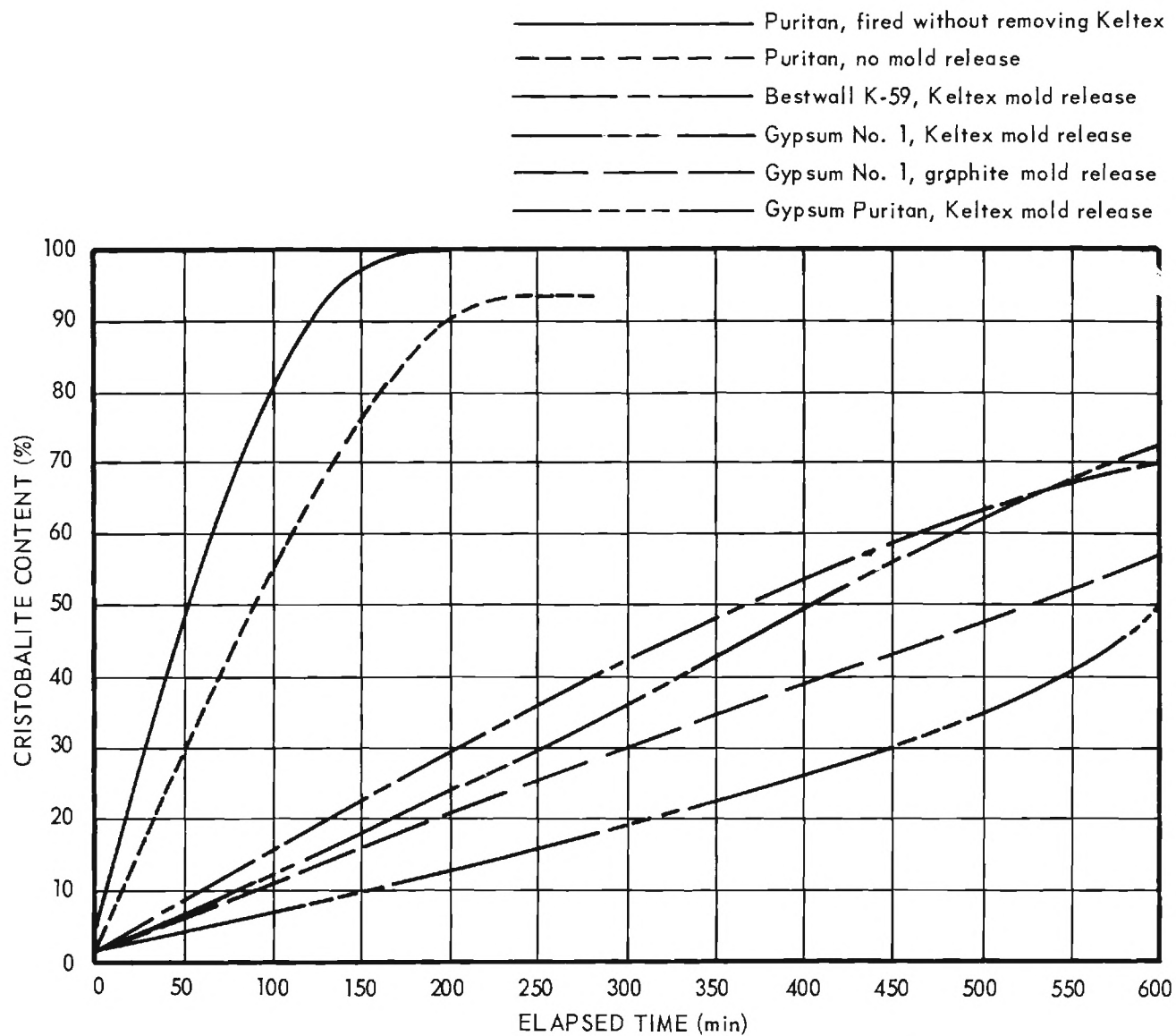


Figure 2. Extent of Surface Devitrification of Slip Cast Fused Silica at 2200°F.

retained in the film combine to give a higher surface devitrification rate than is obtained if no mold release is used at all.

Although Figure 2 indicates that surface devitrification is more rapid with No. 1 or K-59 plaster, the devitrification is not accelerated throughout the casting. Castings produced in molds of these plasters did not show any greater tendency toward bulk devitrification, surface spallation, or lower strength than those from Puritan molds. As a result, it appears safe to say that any of the three plasters tested, or any similar plaster, will be suitable for slip-casting fused silica. If the maximum precautions are to be taken to produce the best possible castings, however, Puritan plaster should be selected in spite of the fact that the concomitant lower rate of surface devitrification has not been proved to yield any demonstrable advantage.

§ 3.7 Casting the Working Mold

Preparation of the working mold for slip-casting fused silica does not involve any special techniques not associated with plaster mold preparation for any other process. The design of plaster molds is more an art than a science. Only a few guiding principles may be stated.

In evaluating the working mold design, the low drying shrinkage of slip-cast fused silica should be recalled. Since this shrinkage is less than one per cent, the silica casting will not separate from the mold wall and fall out of the mold as do castings produced from other slips. As a result, the mold must be designed to separate into as many parts as are required to facilitate removal of the casting. This presents no real difficulty, however, and facility in dealing with this characteristic is developed quickly by pouring a few trial castings.

While the working mold should be cast in as many parts as required to permit easy removal of the casting, the smallest number of parts possible should be used since fewer parting lines will result in better reproducibility of strength, though no higher average, in the castings. For example, rings cast in two piece molds showed a greater reproducibility of strength at the 99 per cent level of confidence than rings cast in four piece molds although the average strengths of the two types were not significantly different (30).

Problems which might arise in casting the working mold should be considered in designing the master pattern. For example, to illustrate the mold forming process, suppose an hourglass-shaped specimen is to be cast. Producing the working mold will be simplified if the master pattern can be parted along a line of symmetry. In machining the pattern, two bars of the pattern material are ground on one face and joined by means of pins or blind tapped screws. The composite rod is then chucked in a lathe and aligned so that the common face between the two halves of the rod is on the center of rotation. The hourglass shape is machined from the composite bar. The pattern is now separated and one half placed, resting on the ground surface, on a glass sheet. If screws are used to join the two halves of the pattern, the blind tapped half of the pattern is used in this step. Plaster is now poured around this half of the pattern using metal or plastic strips to form a container around the pattern. After the plaster hardens, the pattern half is removed and the pattern is assembled and replaced in the cavity of the plaster with the blind tapped side of the pattern exposed. A pouring spout core is formed, leading to the pattern, from Plastolene or modeling clay. Three or four index depressions are cut into the first plaster casting using a tapered reamer, a 1/2 to 1-inch ball end-mill, or some similar tool. The mold half is then coated with mold soap and plaster is poured to form the top mold half. After the plaster hardens, the mold is separated and the pattern and pouring spout core are withdrawn and the mold soap is thoroughly removed. When used in casting, the two halves of the mold are put back together and held with rubber bands which may be cut from rubber tire tubes. The index depressions cut into the first half of the mold match the index projections formed in the second half of the mold and the two halves of the mold cavity align perfectly.

Since the type of plaster is not of great importance ^{1/}, the personal preference and experience of the mold-maker may be considered in selecting the exact mix to be used. As a guide, the following-mixing procedure is recommended:

- a. Measure out the desired quantity of plaster and water, using a ratio of 1.25 parts of plaster to 1 part of water, by volume.

^{1/}See § 3.6.

- b. Pour the water into the mixing container.
- c. Screen the plaster into the water, breaking up all lumps.
A flour sifter can be used to advantage in making small molds.
- d. Allow the mixture to slake for five minutes.
- e. Blend mechanically for two minutes at a speed sufficient to provide good mixing but not high enough to entrap air.
- f. Pour immediately.

Plaster mixed according to this procedure will set in approximately 30 minutes.

The only additional guide which can be stated is that the mold wall thickness should be kept roughly constant if convenient in order to equalize the casting rate in all parts of the mold. If a thin section separates a thicker section from the pouring spout, the thin section may be kept from casting closed before the thicker section by wetting that portion of the mold before casting or by providing a smaller mold wall thickness near the thin section. If pressure casting is to be used 1/, the wall thickness should be increased in the region of the thin section.

§ 3.8 Preparing the Mold for Use

Before the mold is used, it should be dried. Overnight drying at approximately 120° F is normally adequate.

One precaution is essential. Since devitrification of fused silica is accelerated by a variety of materials 2/, the utmost care should be exercised to avoid contamination of the casting surface of the mold or of the casting itself. It is advisable for workers to wear disposable polyethylene gloves when handling molds or castings.

A mold release agent should be used for all slip-casting of fused silica. If the casting does not have any projections which must be drawn from deep

1/See § 3.11.

2/See § 6.6.

cavities in the mold, Keltex, produced by the Kelco Company, is quite effective. Keltex is a sodium alginate which forms a water-permeable film. The film adds strength to the casting and facilitates handling. Instructions for using Keltex are supplied with the material.

If the casting does have projections which must be withdrawn from deep mold cavities, a Keltex film will wrinkle during removal and make successful release of the casting almost impossible. In such cases, a graphite mold release is preferable. This release is produced by milling a 1120 gm. charge consisting of 36 per cent Dixon's Micro Fyne graphite, 62 per cent water, and 2 per cent gum arabic (28). The charge is rolled in a one gallon ball mill at 60 rpm for 120 hours, using a 4000 gm. ball charge. A working suspension is produced by 100:1 dilution of this stock slurry with water. To coat a mold, the working suspension is poured in until the mold is filled and then immediately emptied.

The graphite mold release imparts no strength to the casting and more care must be exercised in handling the castings. It does result in very easy release, however, and no difficulty is ordinarily encountered in removing the casting from the mold. Use of the graphite release, for example, permits 6-inch long by 3/4-inch diameter modulus of rupture specimens to be cast in one piece molds and pushed from the molds by a plunger.

After the mold release is applied, the mold is ready for casting.

§ 3.9 The Slip

Fused silica slip is available commercially ^{1/} and there will seldom be any reason for the user to prepare his own. Slip obtained from Glasrock Products, Inc., was used in all the work reported herein.

The commercial fused silica slip is prepared by milling coarse arc-fused grain in water. Slips have also been prepared by dispersing dry milled powder in water. Such a slip has recently been reported by Schulle (17). The principal advantage of wet milling is that the resulting material is characterized by a regular particle size distribution through the submicron range and that some silica is dissolved during the milling. This self-

^{1/}See § 11.7.

generated solution stabilizes the slip, enhances sintering, and provides a more neutral slip.

The characteristics of fused silica slips are listed in Table III.

TABLE III
CHARACTERISTICS OF FUSED SILICA SLIPS

	Wet Milled Slip ¹	Dry Milled Slip ²
Approximate Solids Content (w/o)	83	69
Viscosity (cp)	130	80-120
pH	5.2	1-2

¹Glasrock Products, Inc.

²Schulle (17).

Even with a higher solids content, the silica slip prepared by wet milling shows a viscosity suitable for casting at a pH of 5.2 while the dry milled slip required adjustment of the pH to 1-2 with hydrochloric acid to reduce the viscosity to a suitable level. The lower acidity of the wet-milled slip would decrease the tendency to leach impurities from the mold plaster, minimizing the calcium contamination in the casting as well as prolonging mold life.

The particle size distribution of the fused silica slip is shown in Figure 3 together with the distribution in Schulle's slip for comparison. The distribution of the wet milled slip is seen to be more regular and not as fine as that of Schulle's dry milled slip.

The impurity content of fused silica slip is set principally by the raw material used in its preparation. Some carbon contamination can be expected from the arc melting process used in preparing the fused silica grain and some alumina pickup occurs during the grinding. The impurity content of a typical slip is given in Table IV. This content could, of course, be controlled if necessary, by selection of more pure sand and by grinding with silica or mullite balls instead of alumina balls.

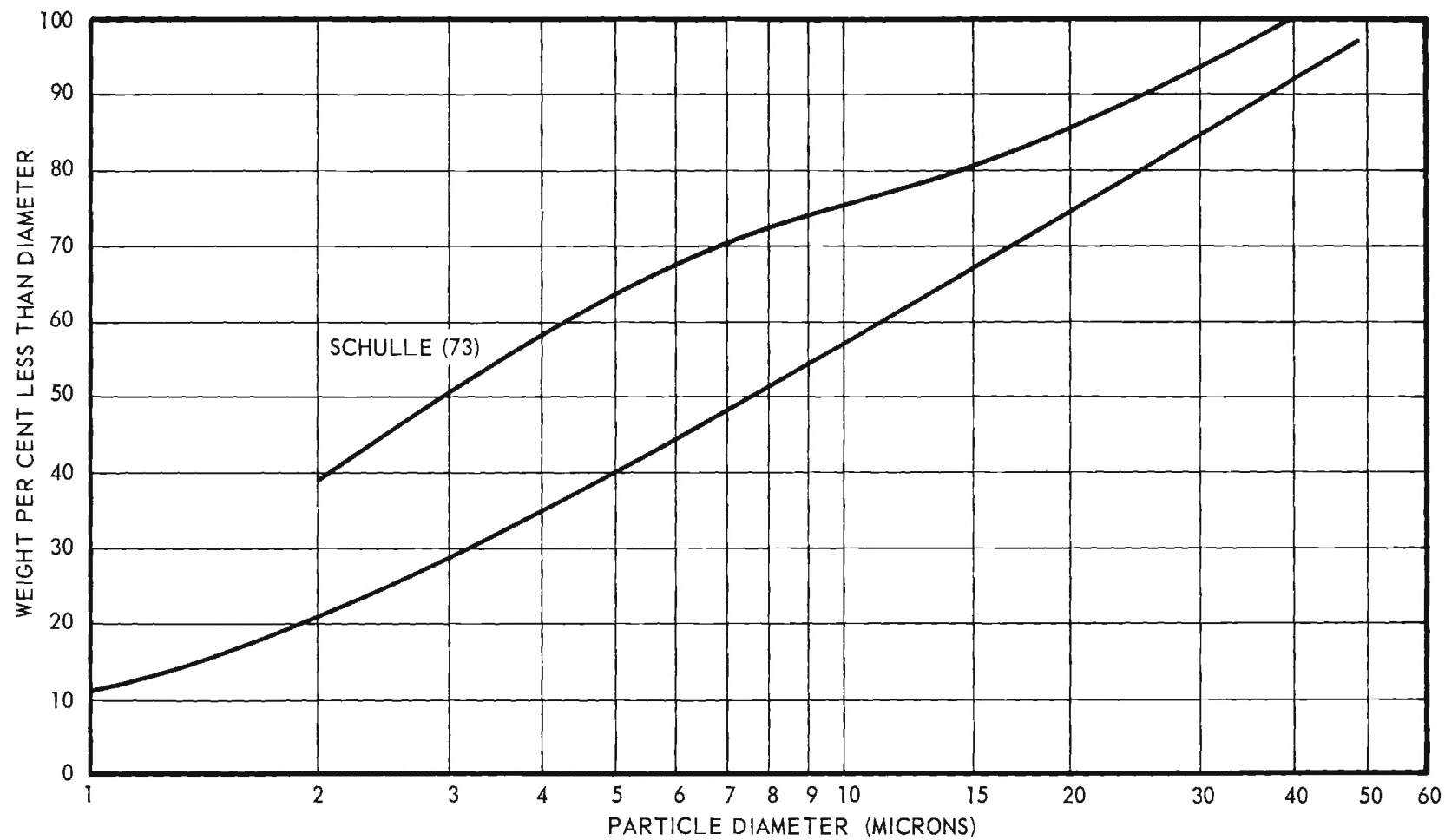


Figure 3. Particle Size Distribution of Fused Silica Slip.

TABLE IV
IMPURITY CONTENT OF FUSED SILICA SLIP

<u>Element</u>	<u>Content (Approximate)</u> (%)
Cu	0.004
Al	0.008
Fe	0.008
Ca	0.001
Mg	0.001
Ti	0.001

§ 3.10 The Casting Process

The silica slip is poured into the dried mold, preferably through a strainer to remove lumps which may have dried around the container top. The filler spout is kept full of slip during the casting process to insure a uniform cast wall thickness. If a hollow casting is desired, the slip is poured from the mold after the desired wall thickness is attained.

Following completion of the casting process, the casting is removed from the mold. Unless the casting contains thin sections separating larger sections, so that shrinkage in the mold would stress the casting, it may be allowed to dry before removal. If the casting is removed before drying, it will have a leathery consistency and reasonable care should be exercised to avoid distortion.

§ 3.11 Casting Kinetics

The rate of casting will be fairly low if only the capillary action of the plaster mold is relied upon to remove water from the slip. This rate may be increased markedly by closing the mold with a gasketed flange and applying pressure to the slip. This effect is shown by Figure 4 which relates the time required to cast a 3/4-inch diameter bar to the applied pressure (34). Application of 20 psig is seen to decrease the casting time by a factor of approximately five.

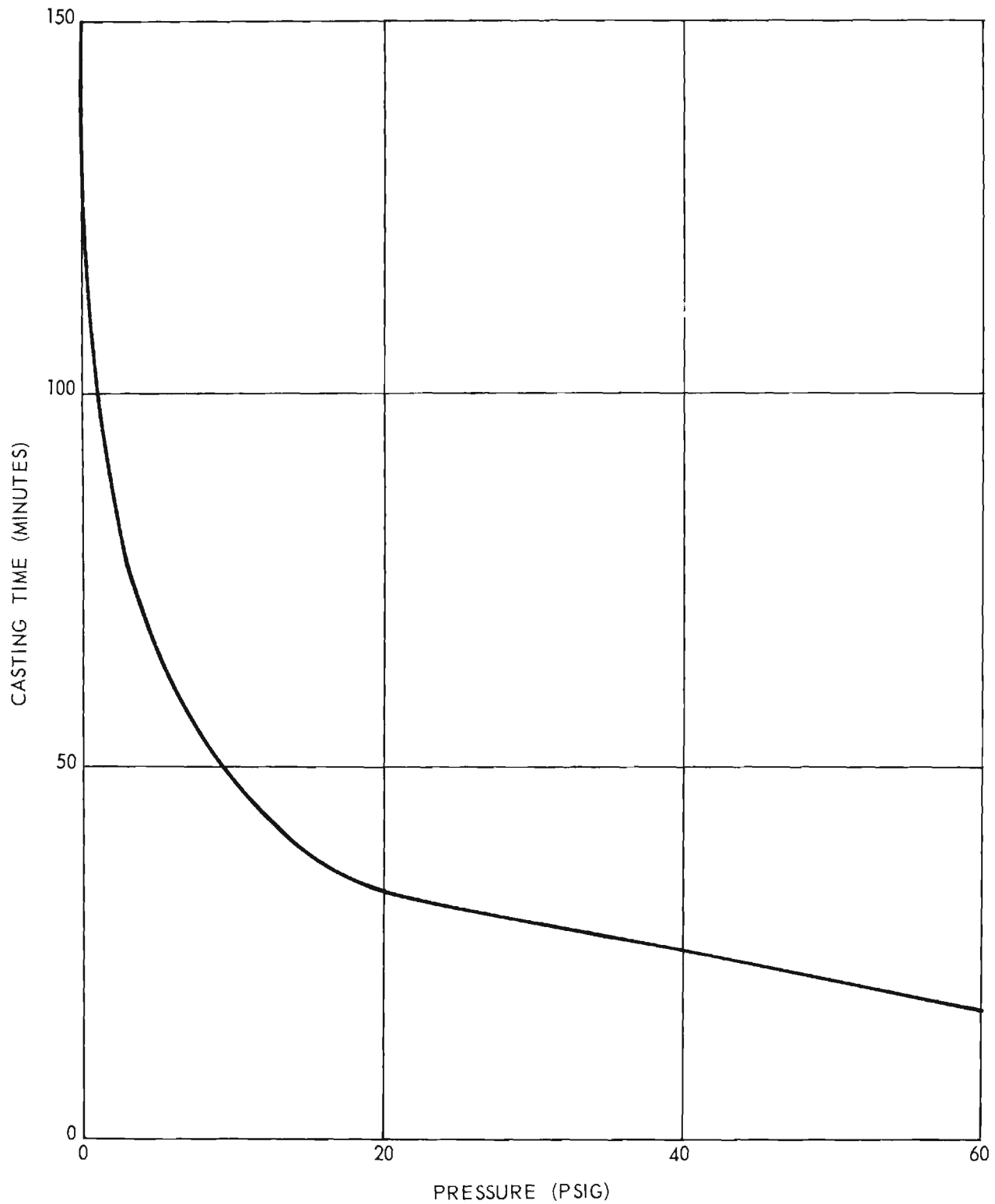


Figure 4. Time Required to Cast a 3/4-inch Diameter Fused Silica Bar as a Function of Applied Pressure.

Application of pressure to the fused silica slip results in behavior much like that of ordinary filtration. This is illustrated by Figure 5 which shows the wall thickness cast against a flat plaster plug, one inch thick, as a function of time and applied pressure (14). If the volume of filtrate collected is replaced by the cast wall thickness, to which it should be directly proportional, the constant pressure filtration equation (3) becomes a parabolic equation.

$$(W + W_c)^2 = K (\theta + \theta_c) \quad 1)$$

where W = cast wall thickness

W_c = cast wall thickness having same resistance to
filtrate flow as the plaster

K = pressure dependent constant

θ = casting time

θ_c = casting time to form the fictitious wall W_c

The values of W_c , K and θ_c can be determined by graphical differentiation of the casting equation (4). Such a plot is shown in Figure 6. The slope of the line is $2/K$ and the intercept is $2W_c/K$. The values of K and W_c were determined and used to solve Equation 1 for θ_c by inserting several datum points from Figure 5. The results are given in Table V.

If the silica casting is incompressible over the pressure range studied, K should be directly proportional to P , except for the case of no applied pressure in which only the unknown capillary pressure force is operative. The values of K/P are also given in Table V for the runs under pressure.

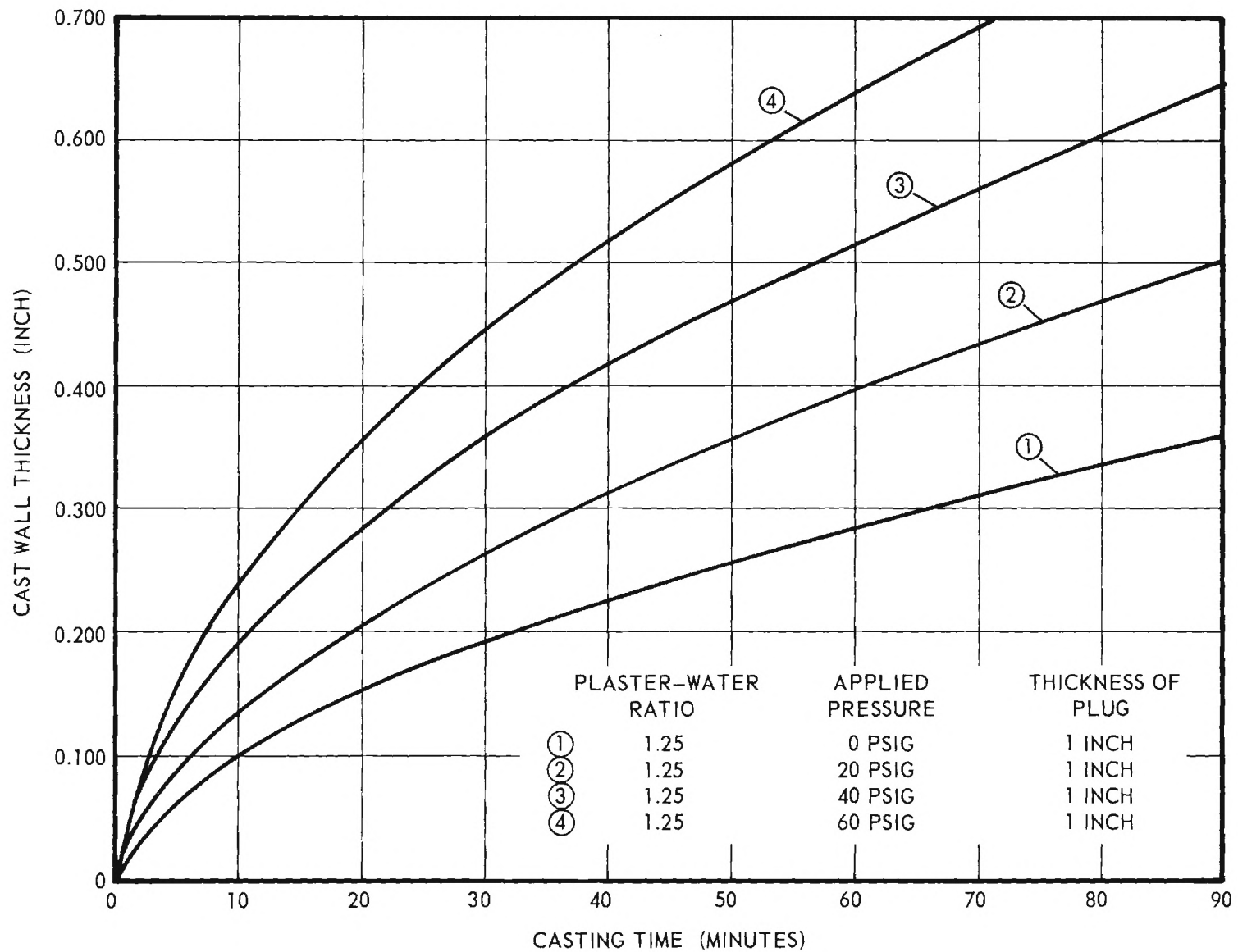


Figure 5. Relation Between Cast Wall Thickness and Time for Fused Silica Slip Cast Under Pressure.

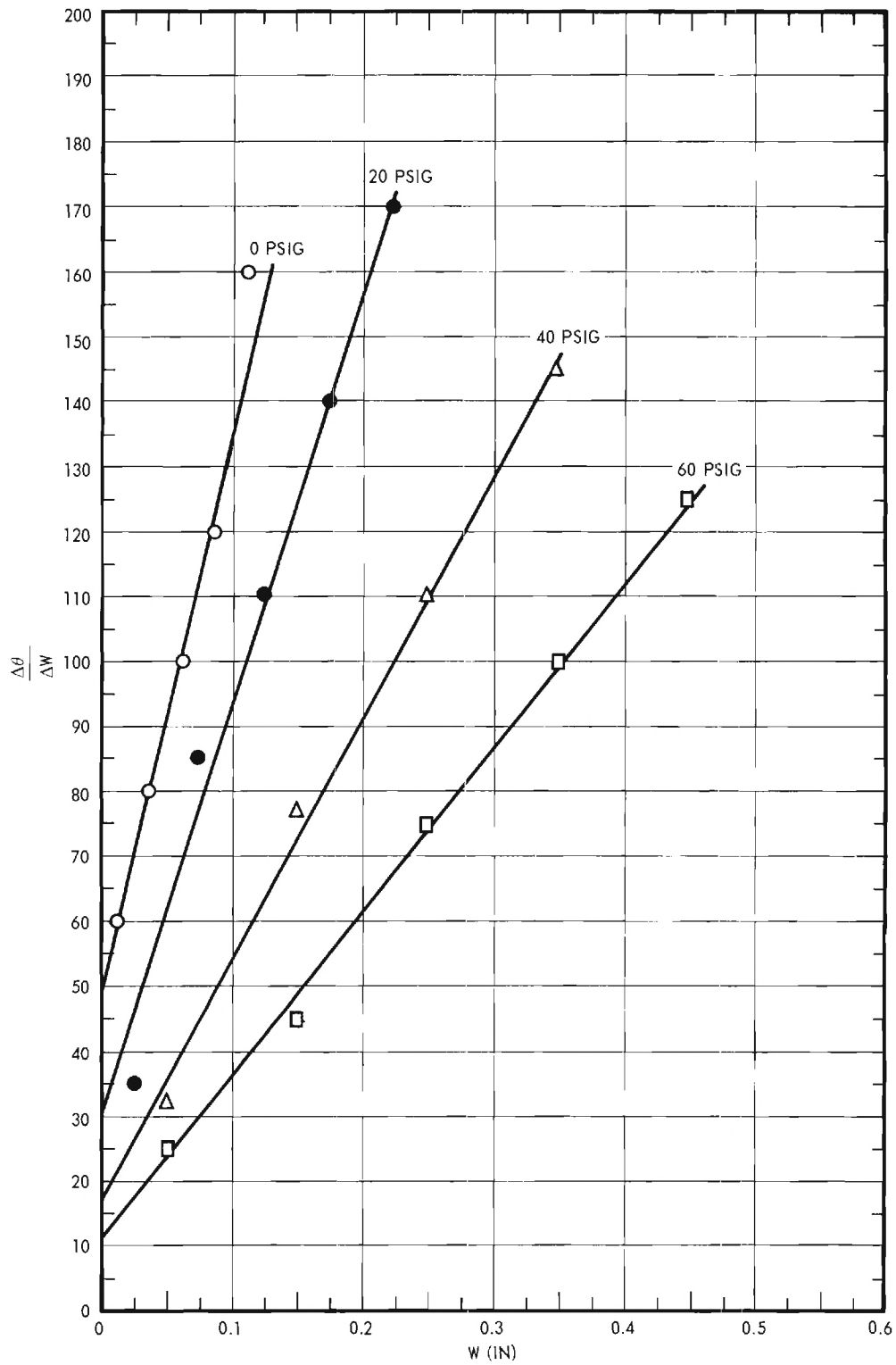


Figure 6. Graphical Differentiation of Filtration Rate Curve.

TABLE V
FILTRATION RATE CONSTANTS FOR SLIP-CAST FUSED SILICA

Pressure (psig)	W_c (inch)	θ_c (min)	K (inch ² /min)	$10^4 \times K/P$ (inch ⁴ /lb _f min)
0	0.0207	-2.66	0.00232	----
20	0.0480	0.65	0.00320	1.60
40	0.0460	0.44	0.00540	1.37
60	0.0465	0.22	0.00810	1.35

Examination of Table V shows that W_c is nearly constant for the pressure runs, that K is approximately a linear function of the applied pressure, and that θ_c is approximately inversely proportional to the pressure. Since θ_c is small, Equation 1 may be rewritten

$$W = 0.012 \sqrt{P\theta} - 0.047 \quad 2)$$

to approximate the slip-casting of fused silica under pressure against a 1-inch thick plaster surface, where

W = cast wall thickness (inch)

P = applied pressure (psig)

θ = time (min)

The negative value of θ_c for the unpressurized casting is due to the fact that the plaster does not represent a resistance but rather is the source of the capillary pressure causing the casting. For casting without pressure, the casting process is represented approximately by

$$W = 0.048 \sqrt{\theta - 2.7} - 0.0207 \quad 3)$$

with the same nomenclature as before.

While Equations 2 and 3 are valid only for a 1-inch thick mold, an

increase in the mold thickness does not produce a radical change in the casting rate either with or without pressure application (15). These equations can be used for any plaster thickness from one to four inches with about 10 per cent accuracy to estimate casting times.

§ 3.12 Preparing the Casting for Firing

After the casting is removed from the mold, it should be dried thoroughly to avoid damage from too rapid moisture evolution during firing. A convenient cycle is overnight drying at about 120° F followed by drying at about 300° F for at least four hours.

If Keltex is used as a mold release, it should be removed thoroughly from the casting before firing. Since Keltex is a sodium alginate and since it traps calcium during casting, the surface devitrification rate of a casting fired with the Keltex in place will be even higher than if no mold release is used at all 1/. If the graphite mold release is used, cleaning the casting before firing is unnecessary. Oxidation of the graphite during firing is apparently quite effective in removing the trapped calcium and no acceleration of surface devitrification is noted 1/.

§ 3.13 Properties of the Unfired Casting

Application of pressure to the fused silica slip during casting decreases slightly the packing efficiency in the casting, resulting in a higher porosity. This may be overcome to some extent by vibration of the mold during casting. Since the extent of the influence of pressure application on porosity is small and the effects on strength cannot be measured, vibration does not appear worthwhile to counteract the application of pressure.

The porosity of dry, unfired castings as determined by air displacement (8) is shown in Figure 7 and the strength is shown in Figure 8 as a function of applied pressure and vibration (35).

§ 3.14 Firing the Casting

Although firing the slip-cast fused silica in air produces more devitrification than firing in an inert atmosphere 2/, the factors which

1/See § 3.6.

2/See § 6.7.

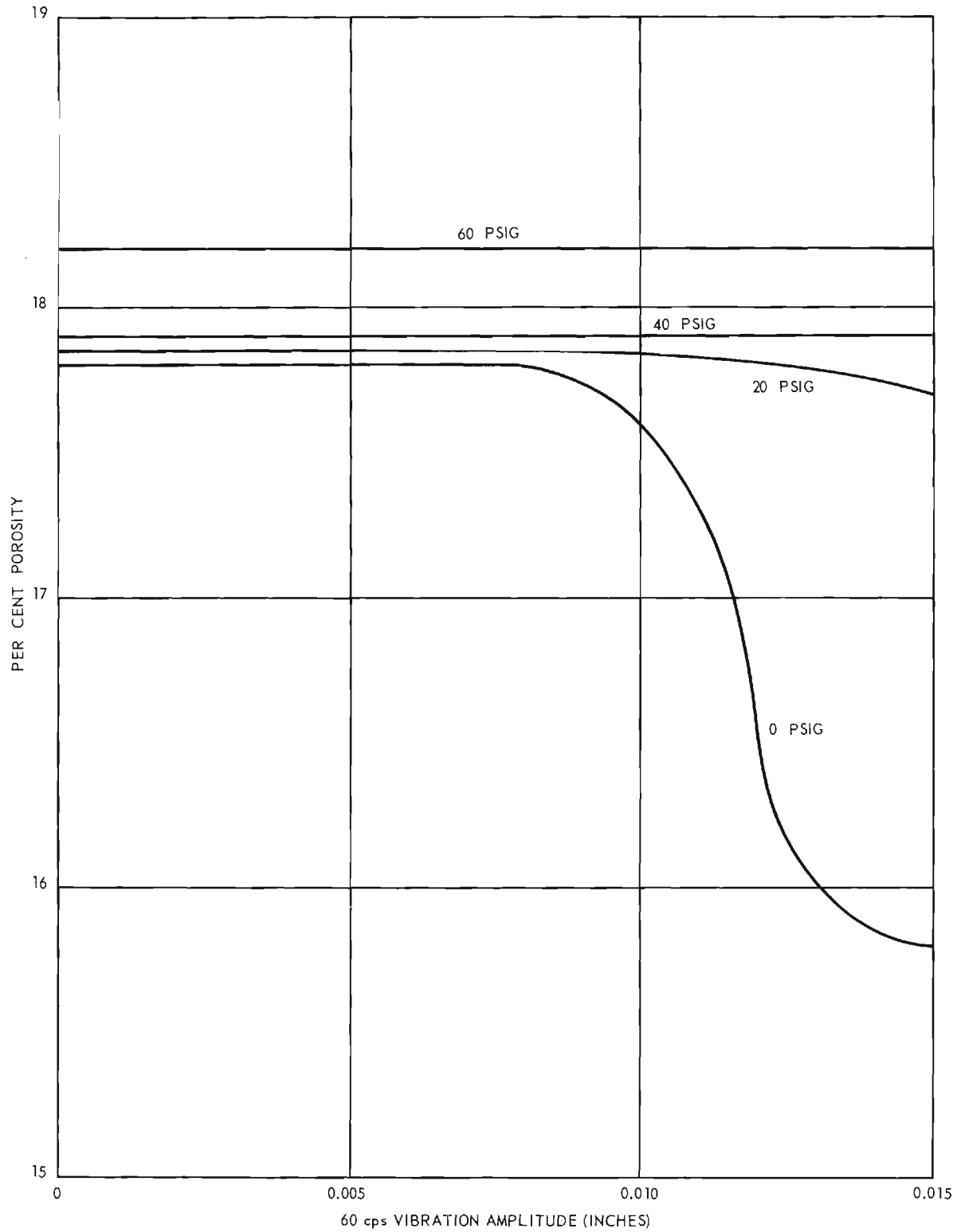


Figure 7. Porosity of Unfired Slip Cast Fused Silica as a Function of Casting Conditions.

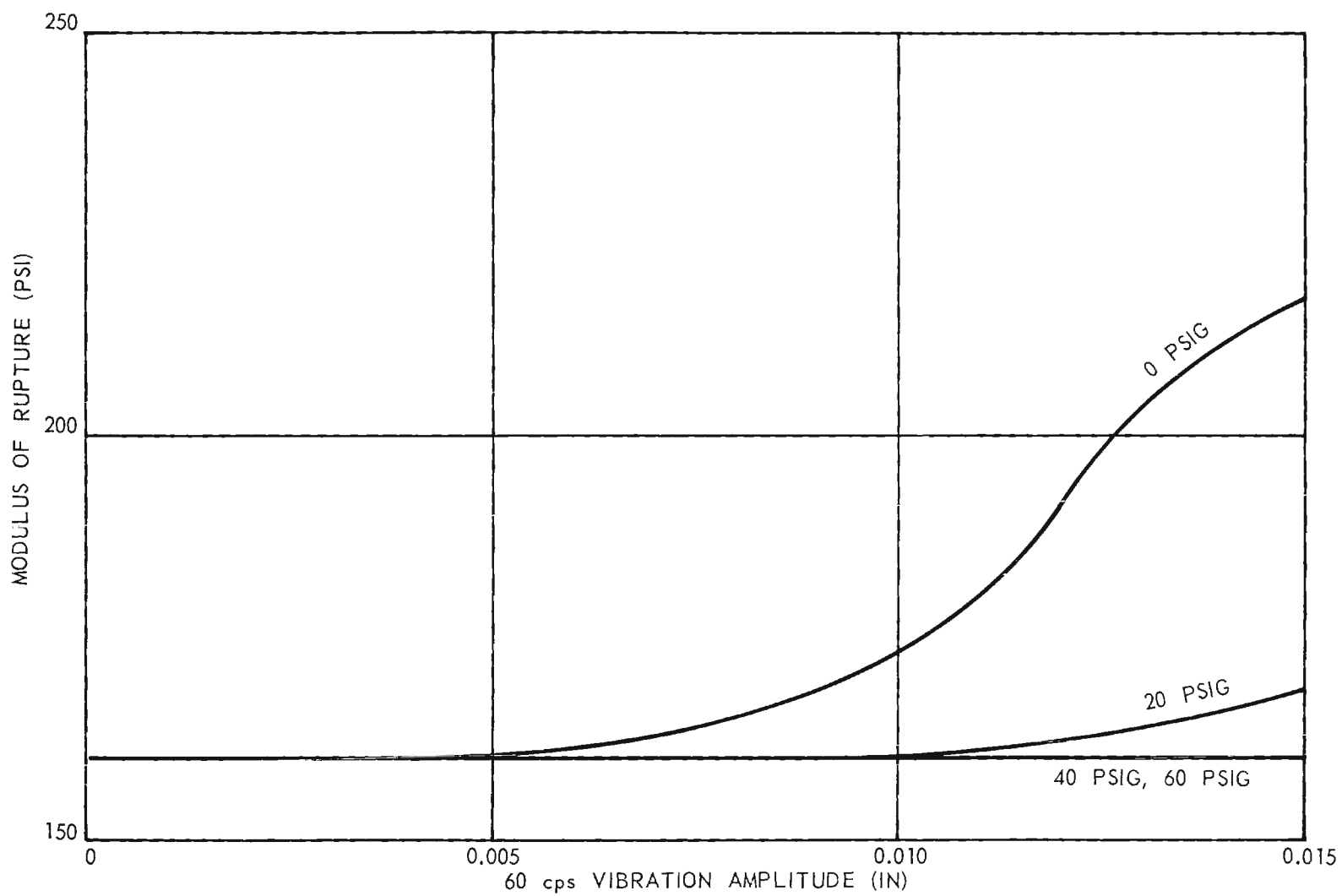


Figure 8. Modulus of Rupture of Unfired Slip Cast Fused Silica as a Function of Casting Conditions.

affect devitrification in fused silica apparently affect sintering in approximately the same manner. As a result, firing in argon suppresses devitrification but it also suppresses sintering. The most rapid sintering is obtained in air or in steam, as discussed in the following section.

Since fused silica has a very low coefficient of thermal expansion, it is resistant to thermal shock. As a result, the usual firing practice is to insert the properly dried casting into a preheated furnace and to air cool after the desired firing time. Slow cooling through the cristobalite inversion does not result in a strength significantly different from that resulting from direct cooling in still air (29).

The proper firing cycle is determined by the results sought. If the casting is to be machined, a bisque firing for two hours at 2000° F will provide sufficient strength for handling and yet avoid sufficient sintering to make machining extremely difficult. For final strengthening, the firing temperature must be such as to permit the casting to strengthen uniformly without undergoing significant devitrification. If a firing temperature of 2200° F is used, the modulus of rupture of the fired casting will be above 4500 psi for firing times from approximately 2.5 to 5 hours 1/. As a result, if a four hour firing at 2200° F is used in an electric kiln, all parts of any casting of reasonable size reach the optimum sintering range. This is recommended as a standard firing cycle.

Modification of the standard firing cycle will be necessary if the casting is unusually large since a longer time will be required for the center section to reach temperature. For a thick casting, the firing conditions may be altered to 12 hours at 2150° F in an electric kiln. This provides a range of optimum sintering from about 6 to 18 hours, providing ample uniformity although the average strength of the casting will not be as high as firing at 2200° F.

If a gas fired kiln is used, in which the products of combustion can reach the firing chamber, the firing cycle must be shortened as a result of effects of water vapor on the rate of sintering 2/. In general, gas kilns

1/See Figure 11, § 3.15.

2/See § 3.15.

should be avoided, in view of the variability of the water vapor concentration in the flue gas, unless the combustion chamber is well isolated from the firing chamber.

§ 3.15 Properties of the Fired Casting

Two rate phenomena govern the properties of fired slip-cast fused silica. The first is the sintering process which has been shown to be by viscous flow (24, 25). The second is devitrification 1/.

As the firing time and firing temperature increase, the casting shows improved sintering and concomitant increases in strength and bulk density. At the same time, however, devitrification occurs. When the casting is cooled after firing, the cristobalite resulting from the devitrification fractures as the cristobalite inversion temperature is passed 2/, and the strength and density decrease. As long as the increase due to sintering exceeds the decrease due to devitrification, the room temperature properties improve. At some point, however, the effects of devitrification will over-ride those of sintering and the room temperature properties deteriorate. The elevated temperature properties, however, are more stable as long as the temperature does not fall below the cristobalite inversion point 3/. The room temperature properties of fired fused silica castings thus reach a maximum with increasing firing time and temperature and then decrease. The location of the maximum for different firing atmospheres is dependent on the relative effects of the atmosphere on the viscosity, hence the sintering rate, and on the devitrification rate. This is illustrated by the effects of argon, air, and steam firing atmospheres on the bulk density and strength of slip-cast fused silica as shown in Figures 9 and 10.

Since steam and air firing produce much more rapid sintering than inert gas firing, the argon firing process was discarded as being too slow for practical use. Detailed studies of the modulus of rupture and void properties, as determined by air displacement (8), were made for firing in air and in steam (33). The results of these studies are shown in Figures 11 through 19.

1/See Chapter VI.

2/See § 6.7.

3/See § 6.8.

The relative rates of sintering in air and steam are compared, for convenience, in Figures 20 through 22 for a firing temperature of 2100° F. From these figures, the advantages of firing in steam are obvious. If speed of firing is of importance, the increased cost of steam firing equipment may be well worthwhile.

In figures 9 through 22, the properties shown are at room temperature. All temperatures and times shown on the curves refer to the firing conditions.

The early stages of sintering produce a significant decrease in the specific surface area of slip-cast fused silica. The changes which follow this initial decrease have not been fully explored and the available data do not show clearly whether or not a minimum is reached. These data are given in Table VI (26).

TABLE VI
SPECIFIC SURFACE AREA* OF SLIP-CAST FUSED SILICA FIRED IN AIR

	Dried Slip:	5.39 M ² /gm		
	Cast, Unfired:	5.24 M ² /gm		
	Firing Temperature			
Firing Time	2000° F	2100° F	2200° F	2300° F
(hr)	(M ² /gm)	(M ² /gm)	(M ² /gm)	(M ² /gm)
0.5	—	—	—	1.78
1	—	—	—	1.49
2	2.74	2.50	1.72	1.34
4	2.48	1.93	1.32	1.09
8	1.04	2.31	1.04	—
16	1.09	2.85	1.09	—

*Determined by the B.E.T. technique of low temperature nitrogen adsorption.

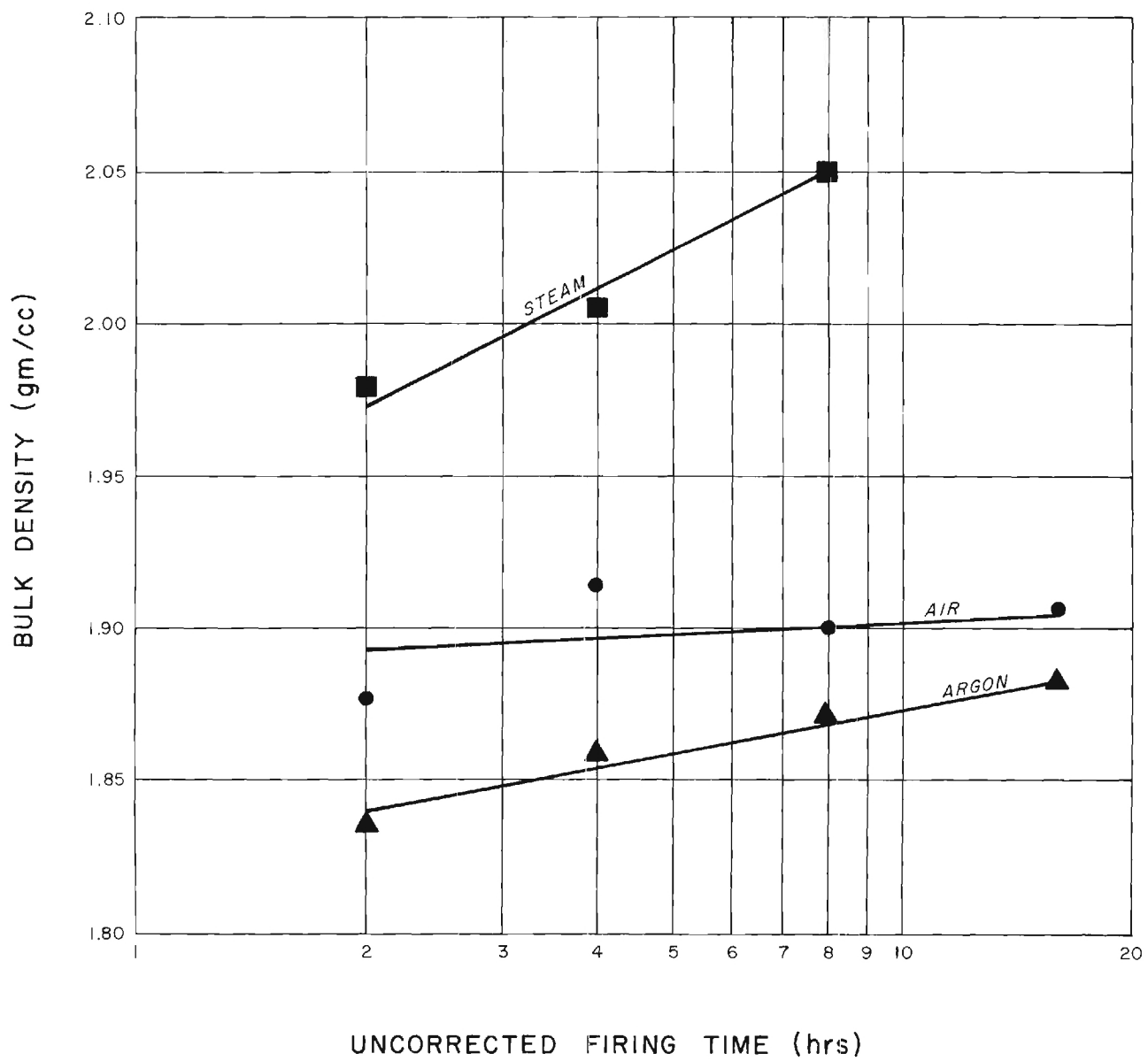


Figure 9. Bulk Density of Slip Cast Fused Silica Fired in Different Atmospheres at 2200 F.

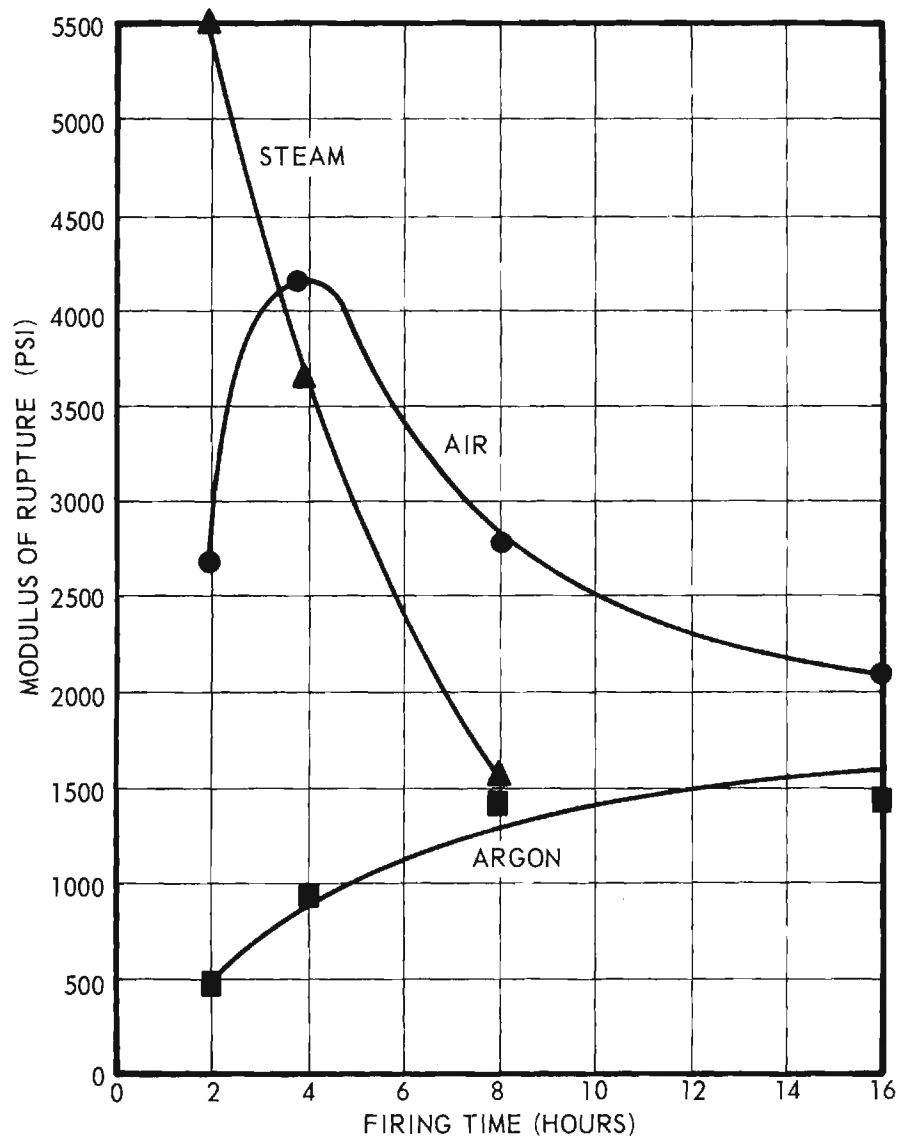


Figure 10. Modulus of Rupture of Slip Cast Fused Silica Fired in Different Atmospheres at 2200°F.

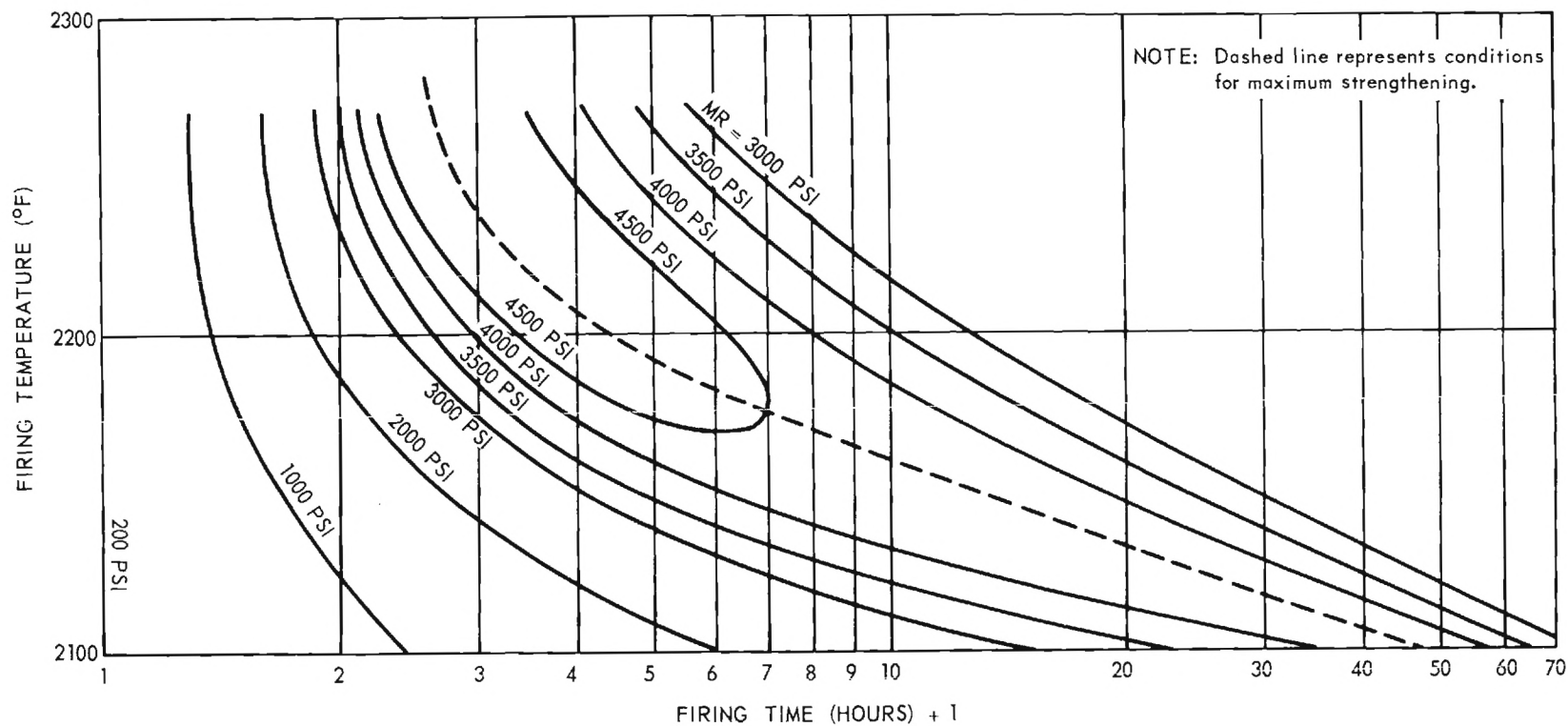


Figure 11. Modulus of Rupture of Slip Cast Fused Silica Fired in Air at One Atmosphere.

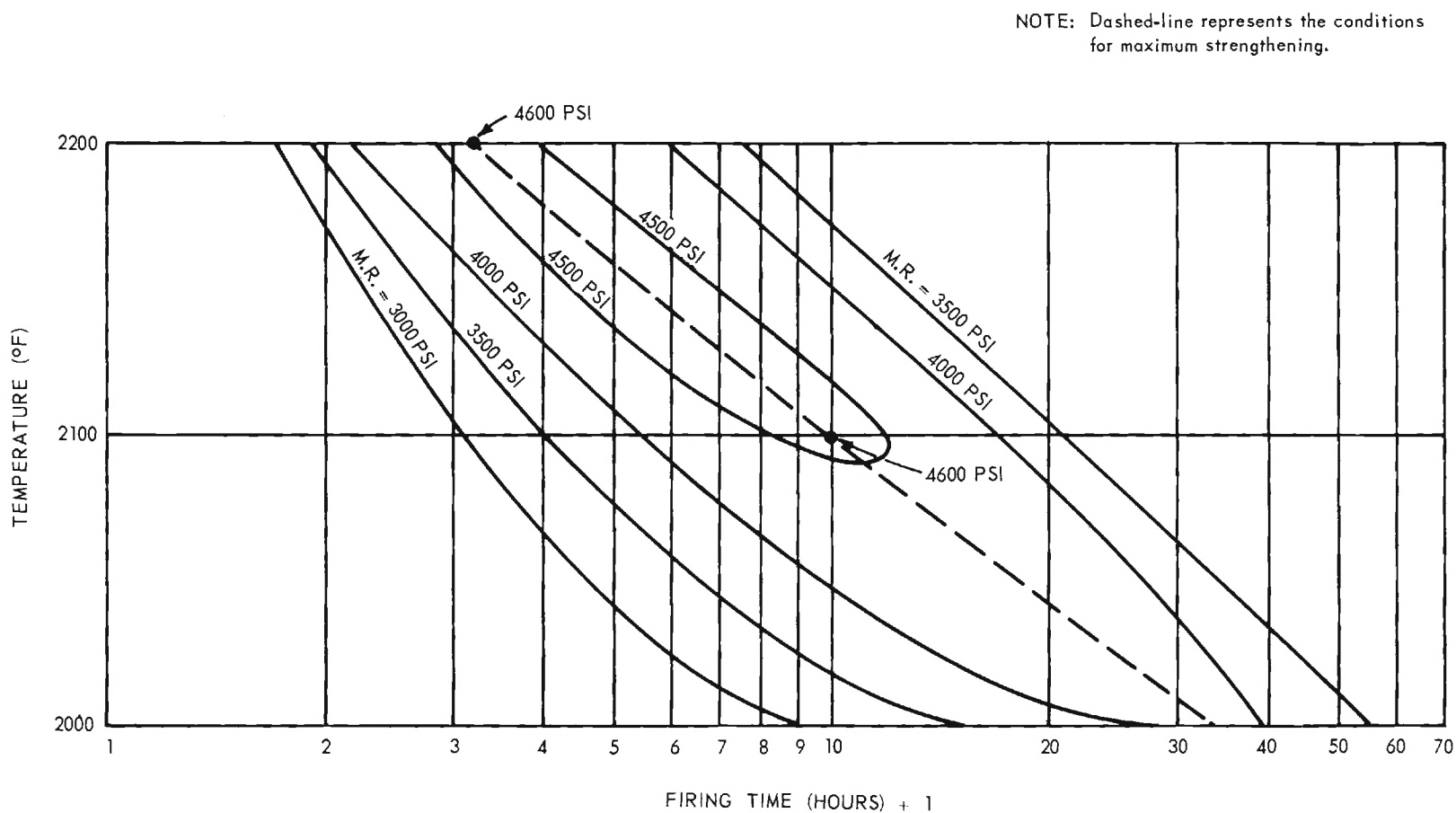


Figure 12. Modulus of Rupture of Slip Cast Fused Silica Fired in Steam at One Atmosphere.

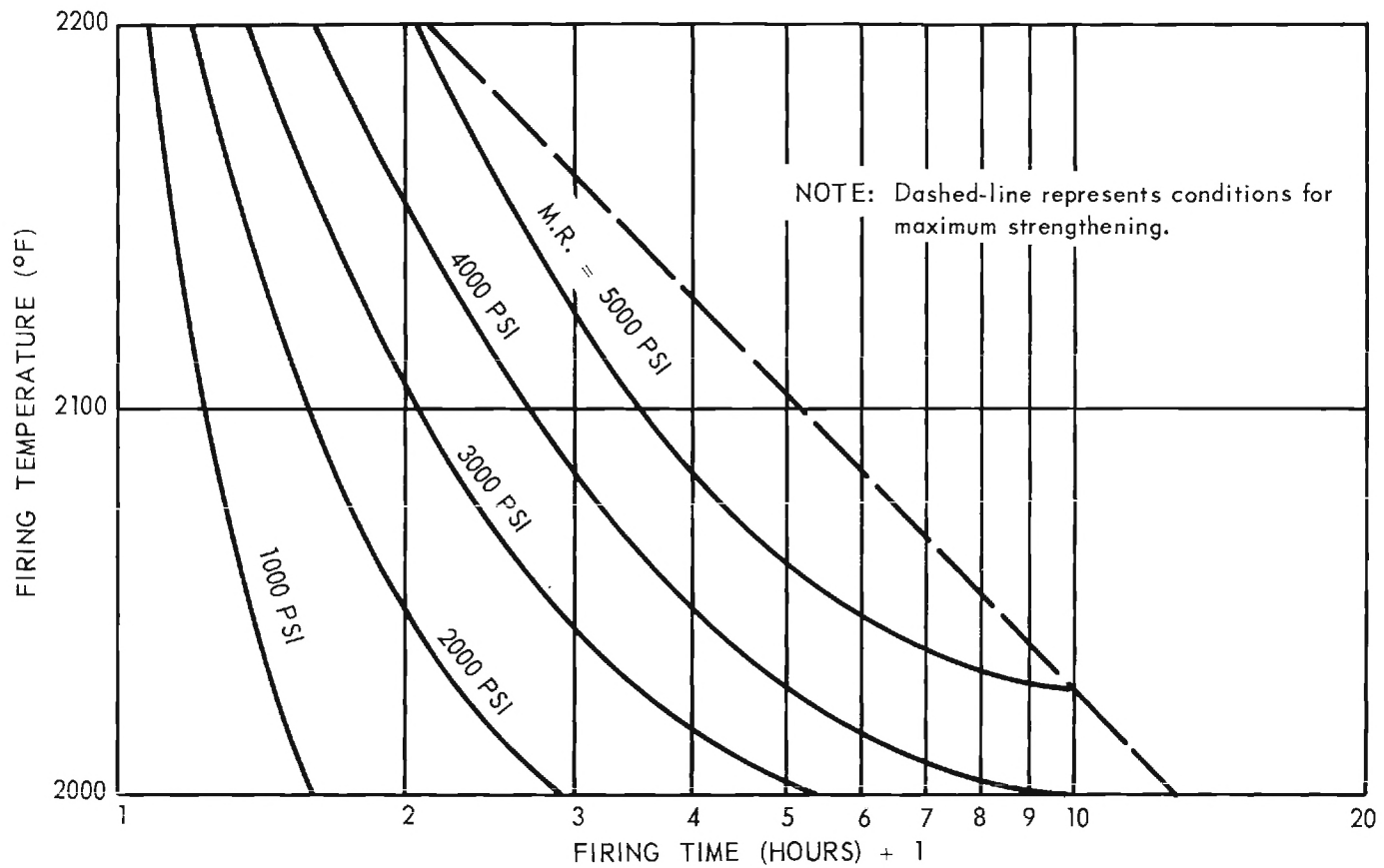


Figure 13. Modulus of Rupture of Slip Cast Fused Silica Fired in Steam at Two Atmospheres.

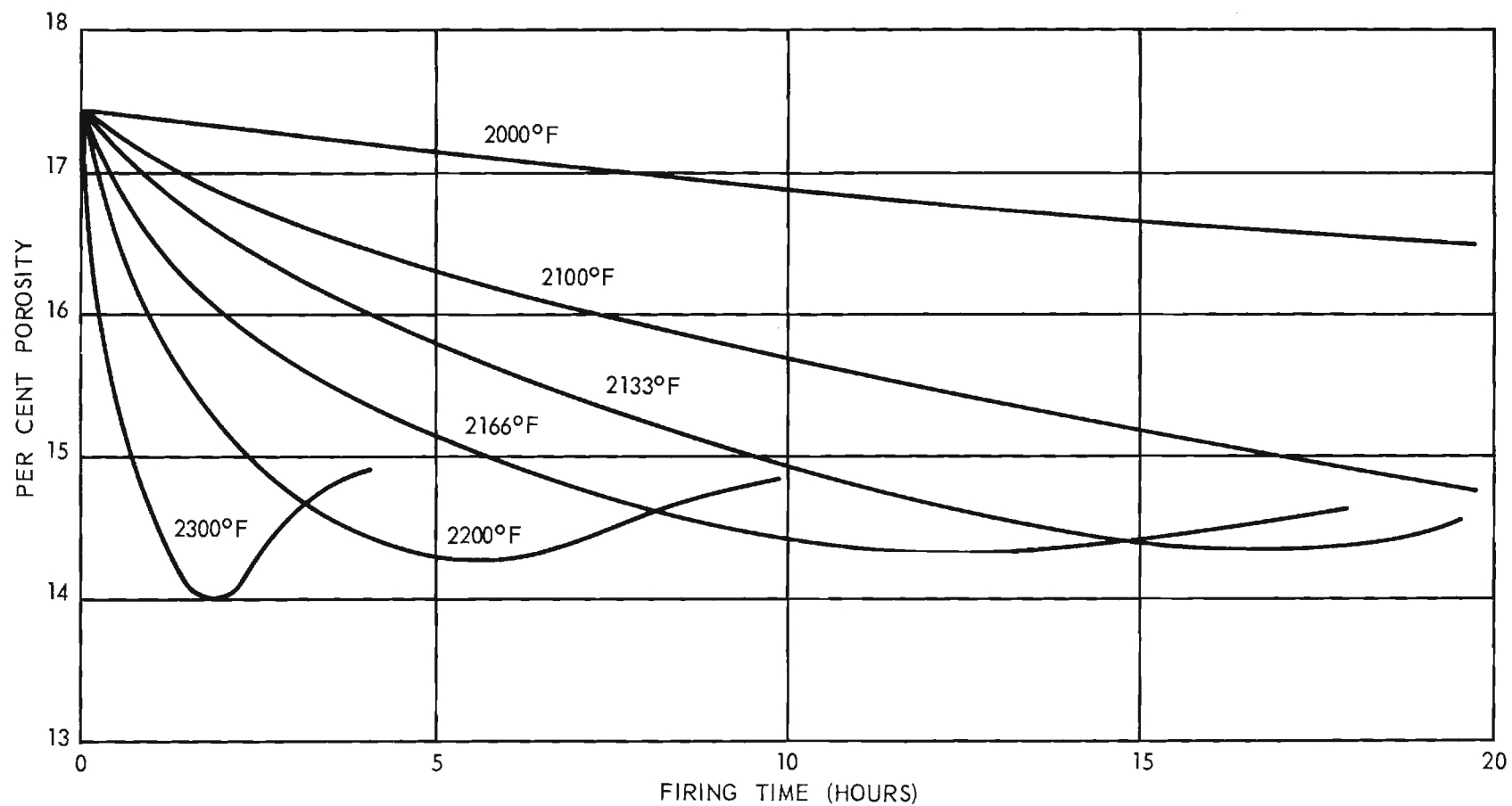


Figure 14. Porosity of Slip Cast Fused Silica Fired in Air at One Atmosphere.

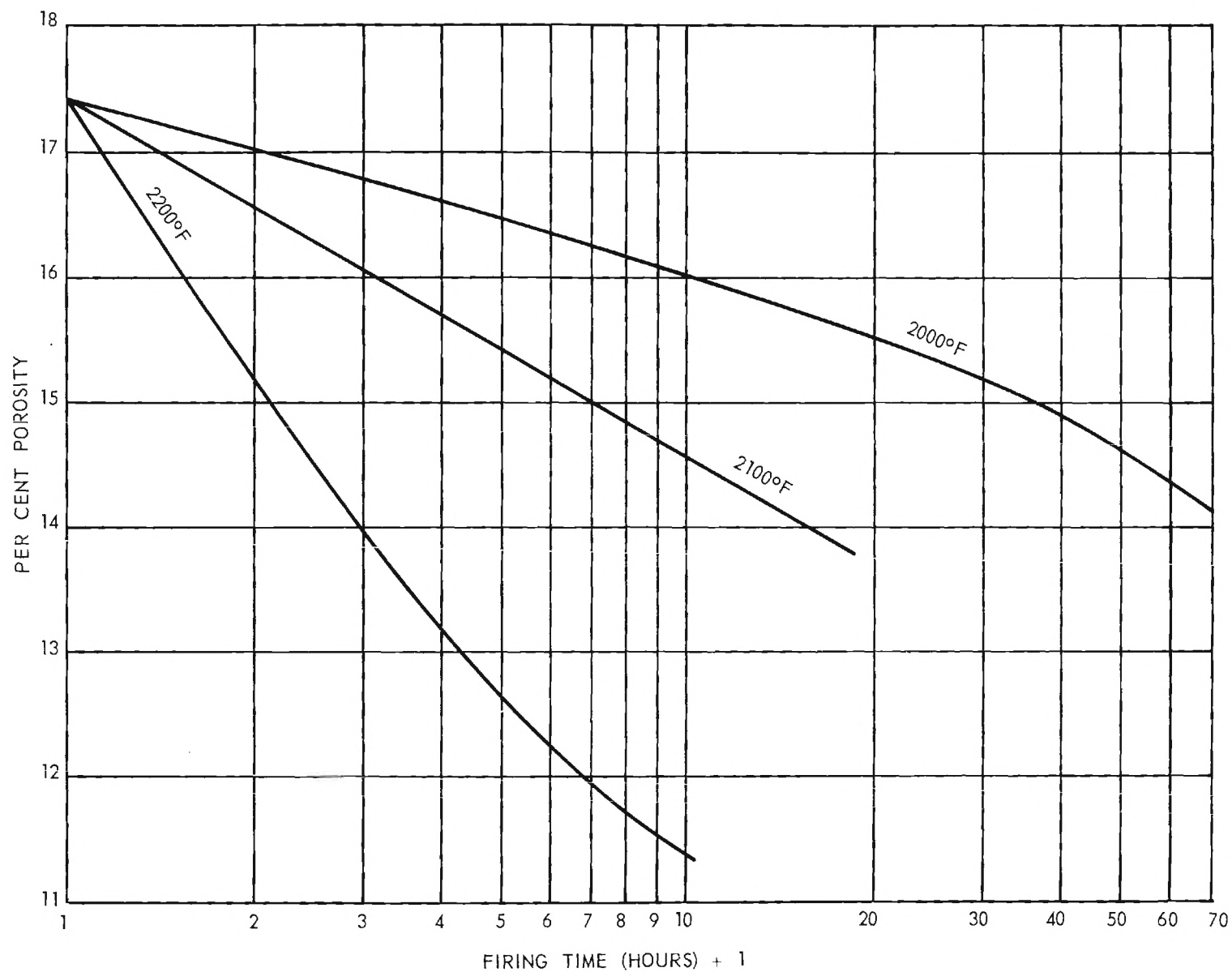


Figure 15. Porosity of Slip Cast Fused Silica Fired in Steam at One Atmosphere.

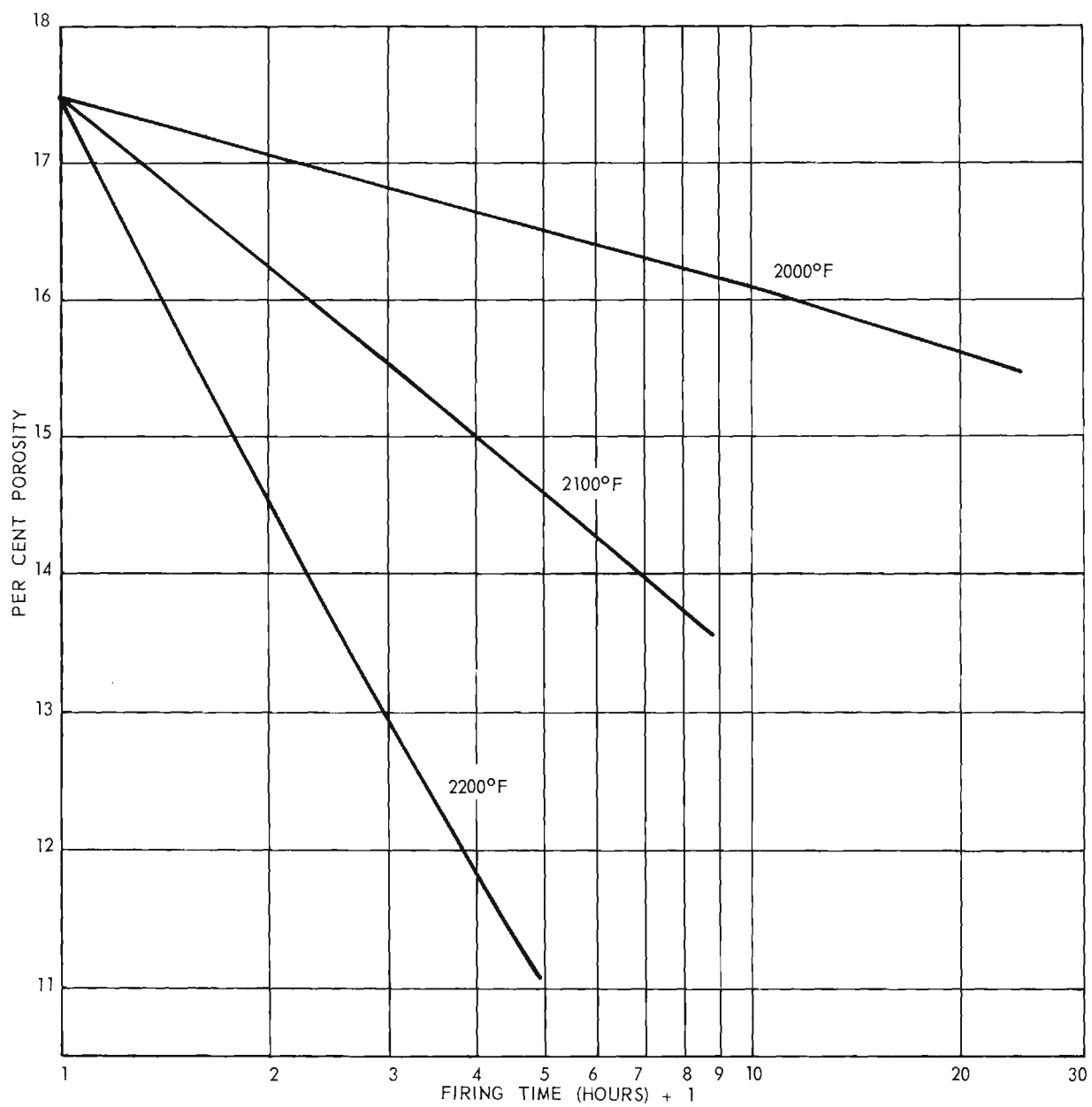


Figure 16. Porosity of Slip Cast Fused Silica Fired in Steam at Two Atmospheres.

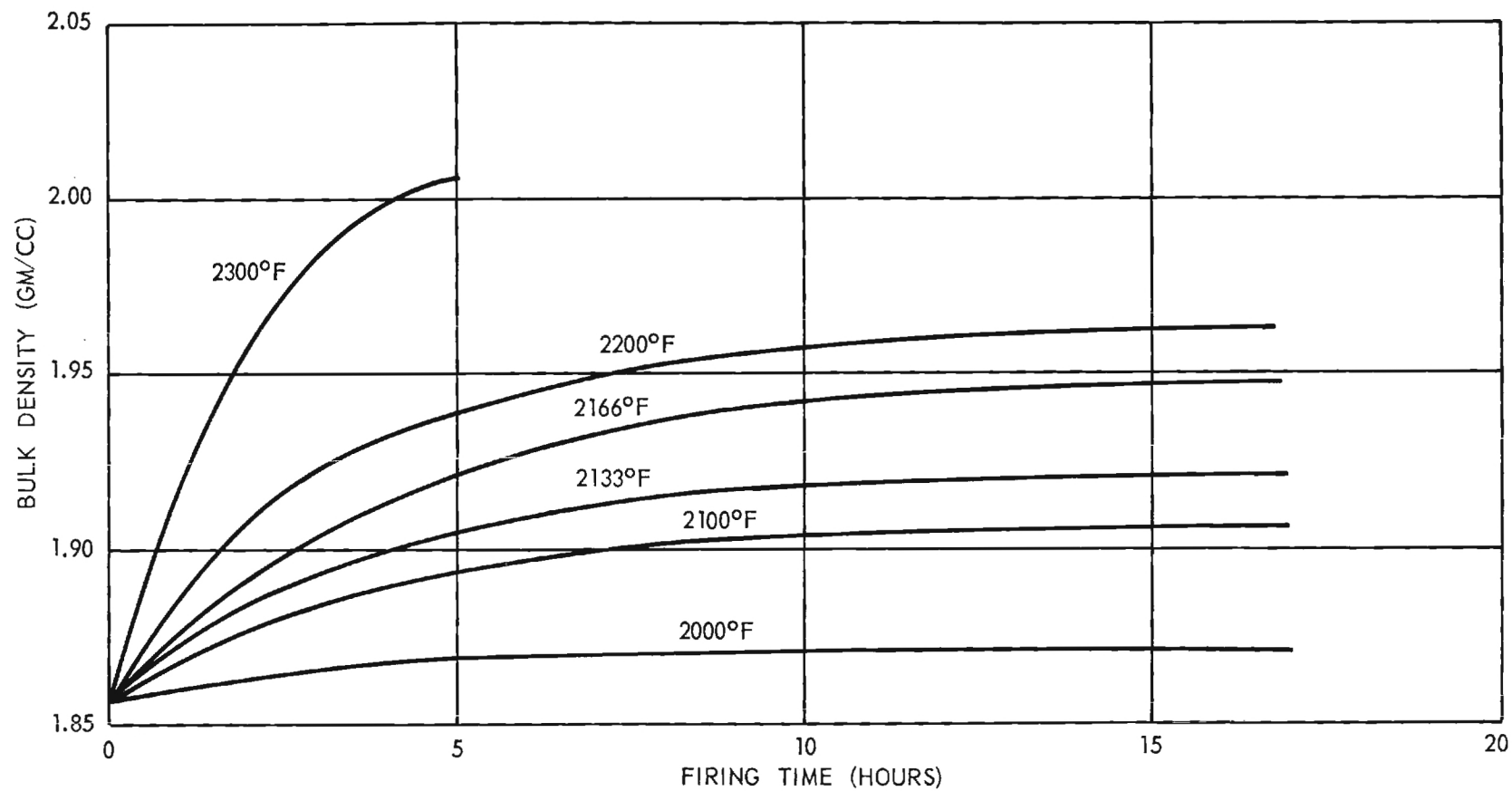


Figure 17. Bulk Density of Slip Cast Fused Silica Fired in Air at One Atmosphere.

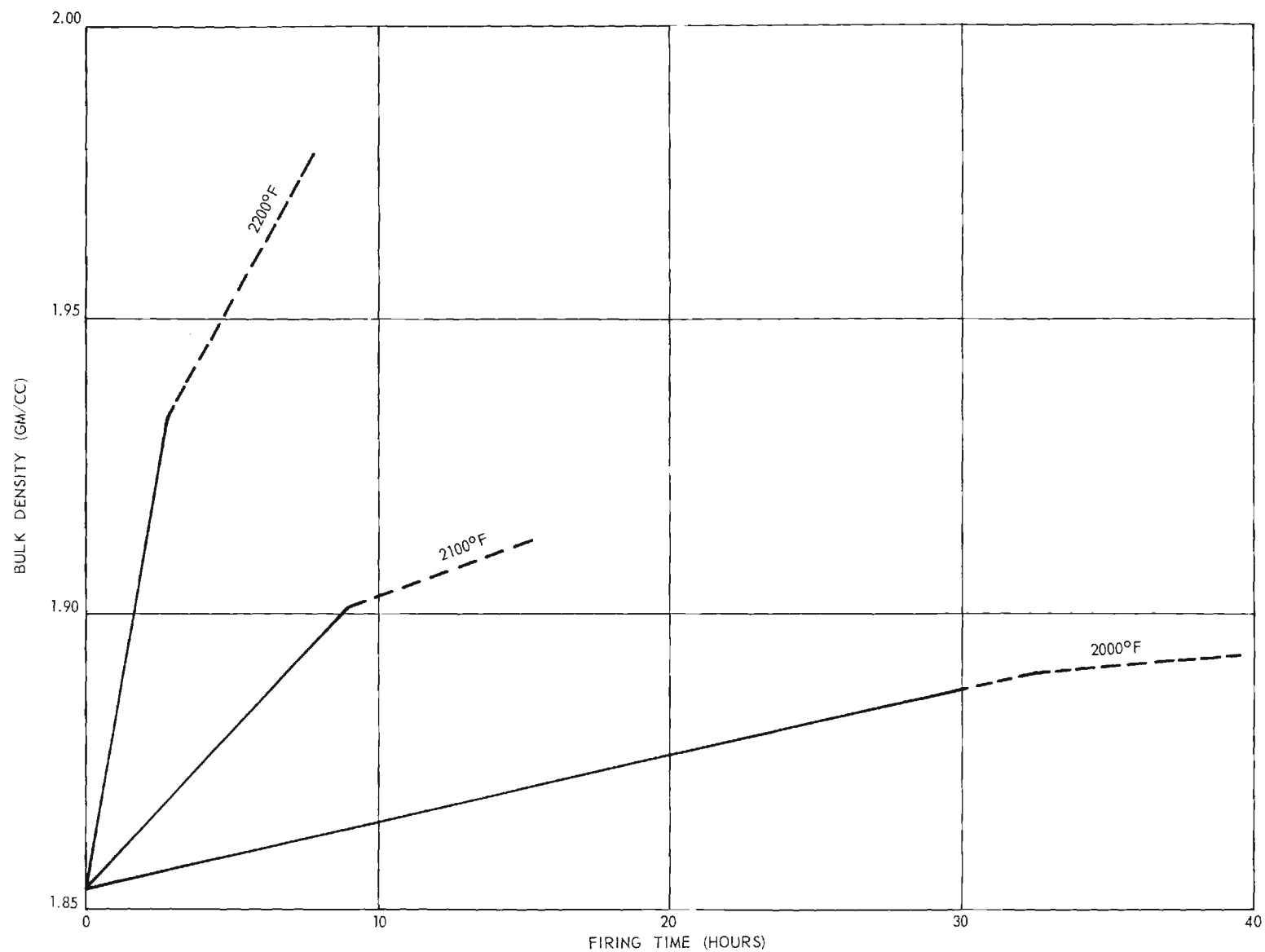


Figure 18. Bulk Density of Slip Cast Fused Silica Fired in Steam at One Atmosphere.

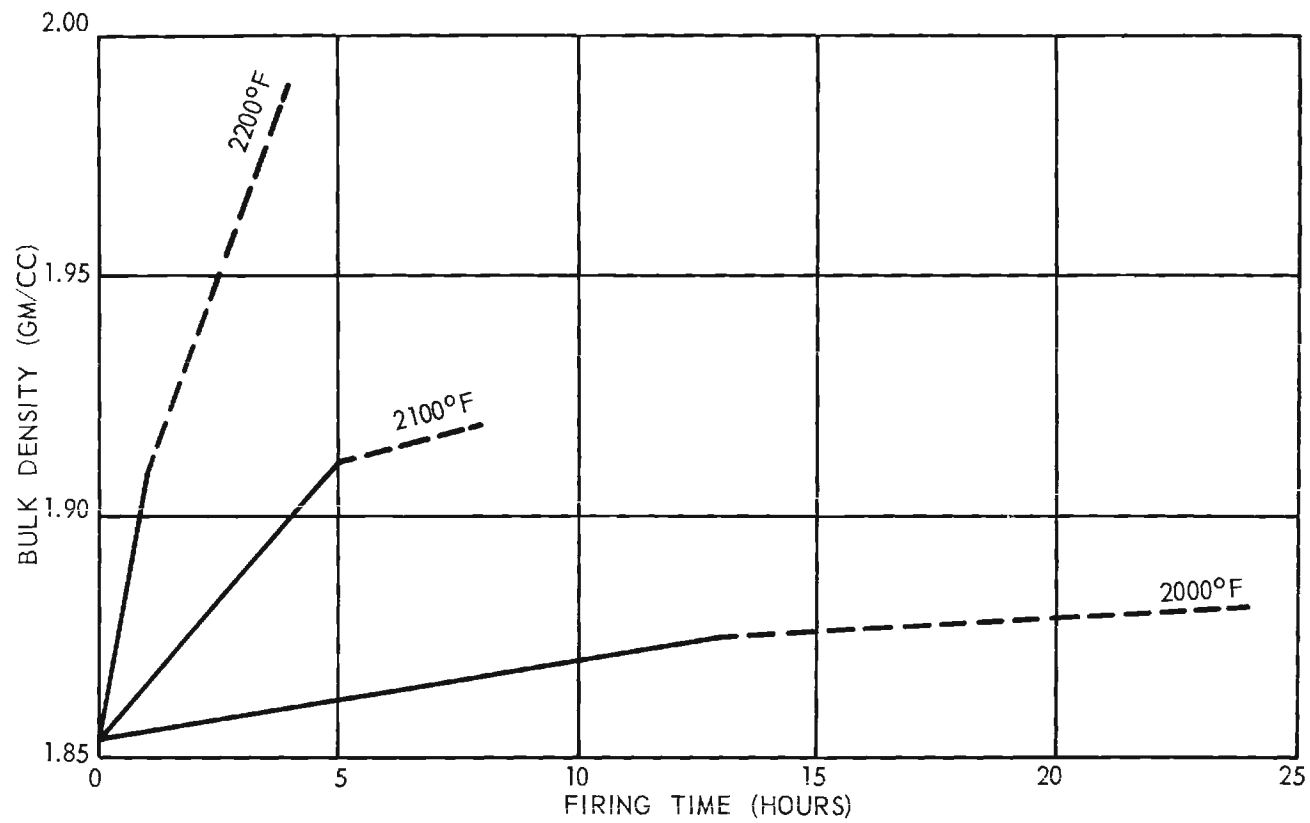


Figure 19. Bulk Density of Slip Cast Fused Silica Fired in Steam at Two Atmospheres.

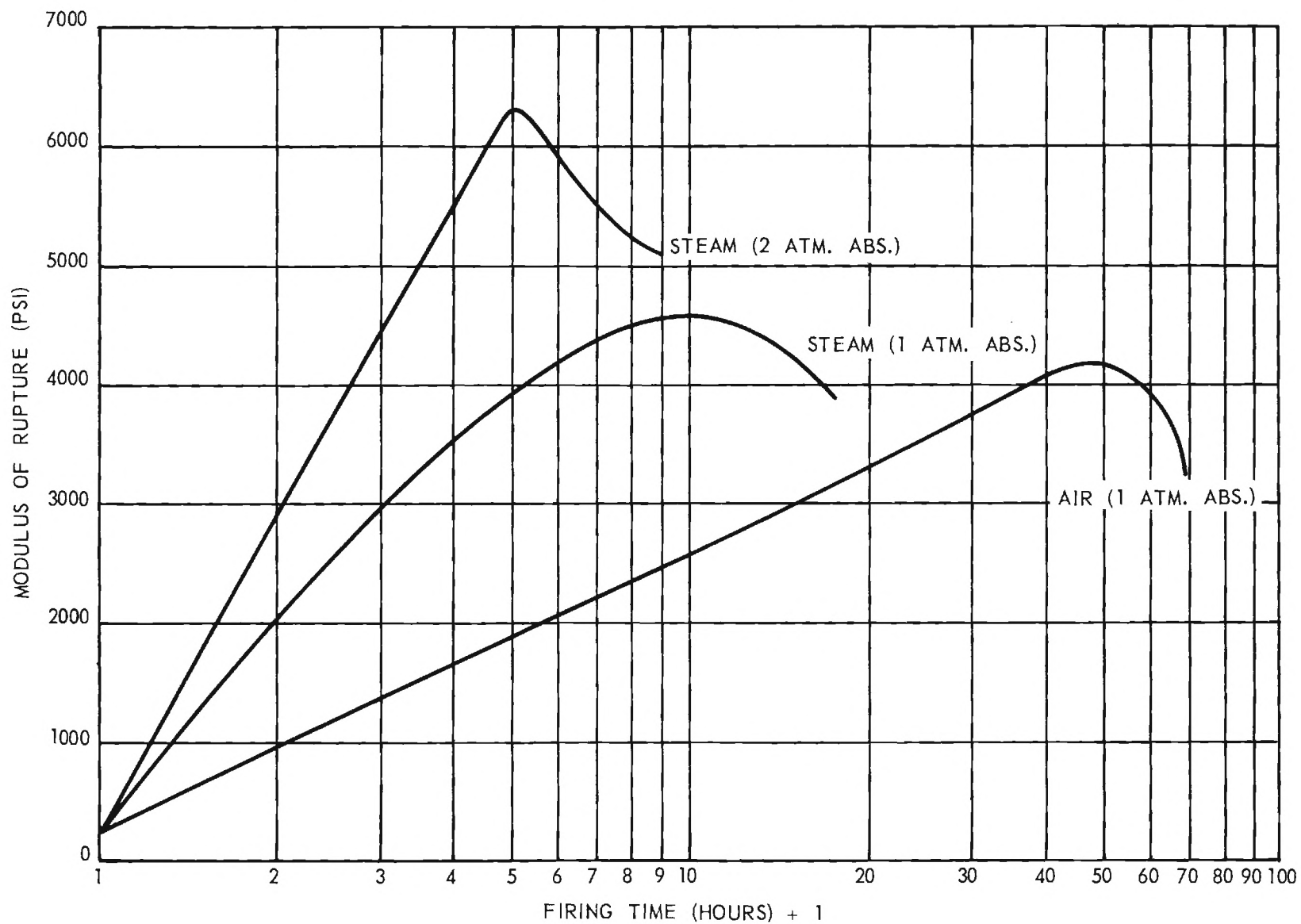


Figure 20. Comparison of Modulus of Rupture of Slip Cast Fused Silica Fired in Air and in Steam at 2100 F.

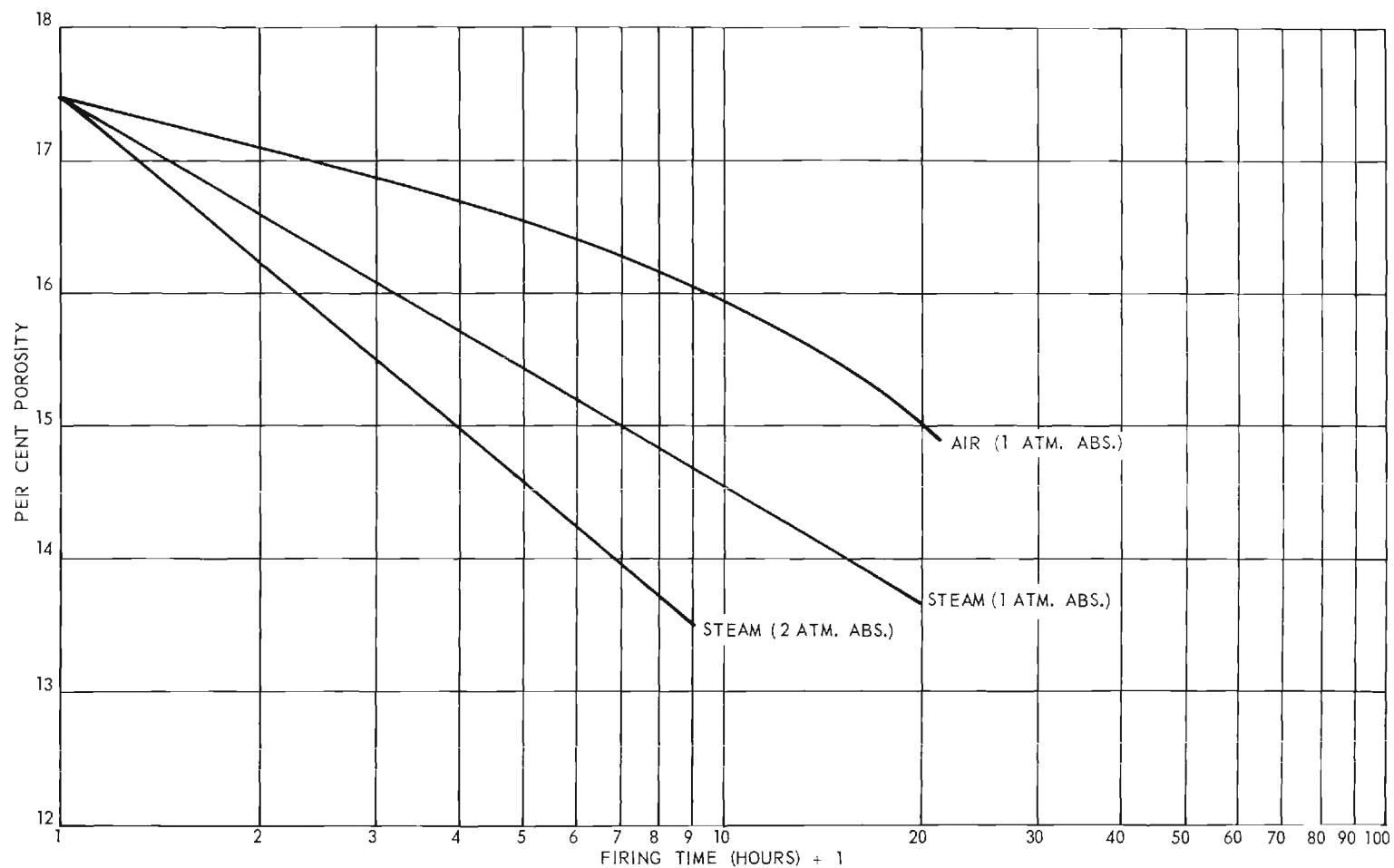


Figure 21. Comparison of Porosity of Slip Cast Fused Silica Fired in Air and in Steam at 2100°F.

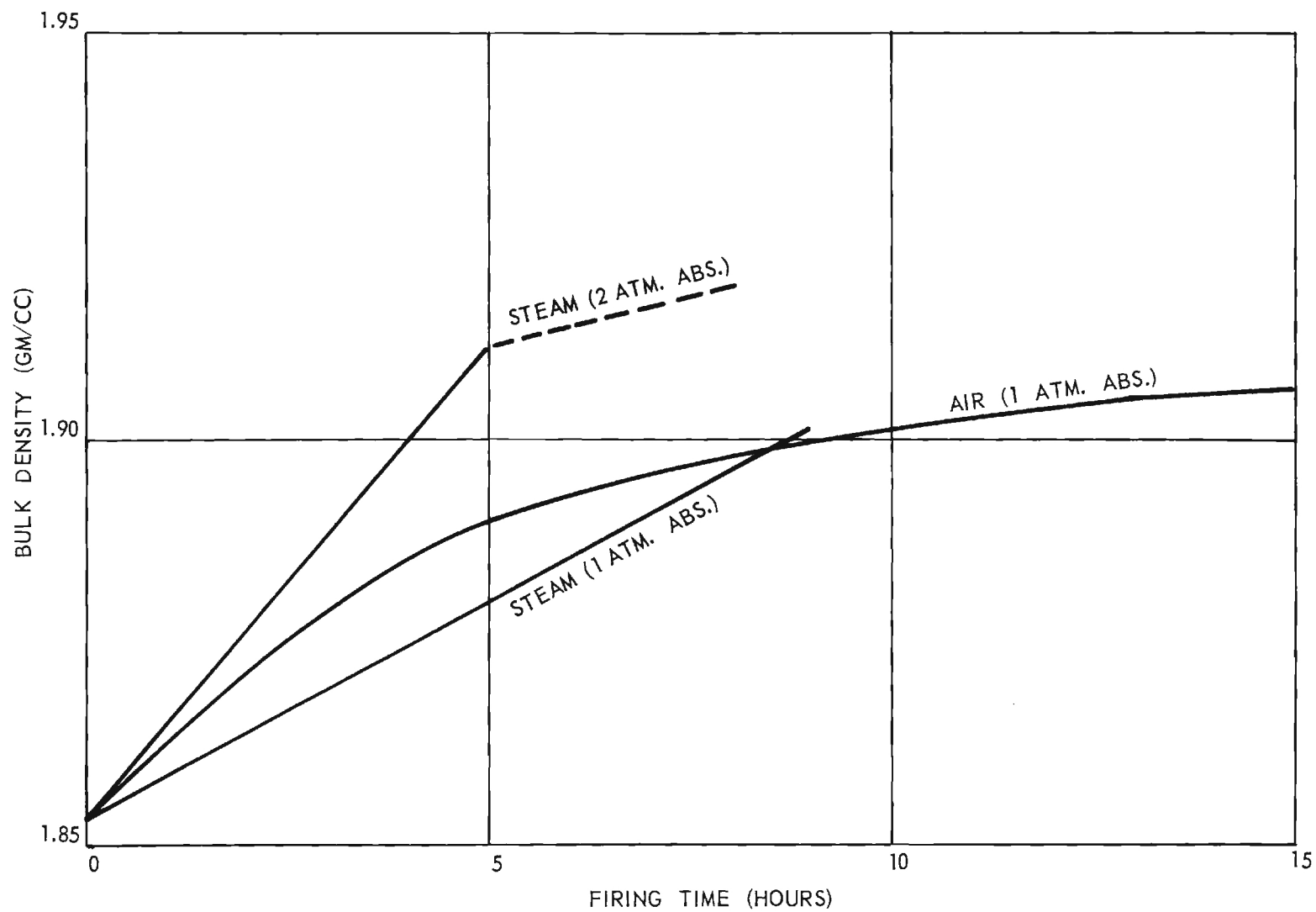


Figure 22. Comparison of Bulk Density of Slip Cast Fused Silica Fired in Air and in Steam at 2100°F.

§ 3.16 Joining Slip-Cast Fused Silica

If the desired configuration is too large or too complex to be cast in a single piece, several component castings must be joined. Although welding could probably be applied, as in glass-working of fused silica, the porosity of slip-cast material would be troublesome since excessive shrinkage would occur. In addition, the technique is of limited utility since welding of closed contours is extremely difficult. Two alternate joining techniques are available, joining during casting and cementing.

Castings of fused silica are porous enough to absorb a small amount of moisture in the dried or fired condition. As a result, if a casting is exposed to slip, a small amount of silica will be drawn onto the surface of the casting. This secondary deposit will sinter to the casting during firing, forming a "metallurgical" bond of high strength. The utility of this method is demonstrated by the one piece slip-cast heat exchanger shown in Figure 23 (26). The center tube was first cast in a cylindrical cavity mold, allowed to dry for a few minutes, and placed in a second mold having the configuration of the shell. The mold was then filled with slip and emptied after the desired wall thickness had cast. During the casting, enough silica cast onto the tube to form an integral bond with the shell casting and a leak-tight joint was formed on sintering.

Slip-cast fused silica may be cemented with any of the commercial refractory cements. In general, cements using a sodium silicate binder should be avoided since the sodium will accelerate devitrification in the joint region. Such devitrification will, however, be limited since migration of the sodium from the cement to the silica is not rapid.

Cement specially prepared for use with fused silica is available commercially 1/. This cement is based on fused silica powder bonded with organo-silicates. Upon air firing, the organo-silicate decomposes to form silica, giving an uncontaminated joint. An acceptable substitute can be prepared by mixing ethyl silicate with fused silica slip (12). This cement yields a shear strength of about 120 psi after maturing at 1800° F.

1/See § 11.7

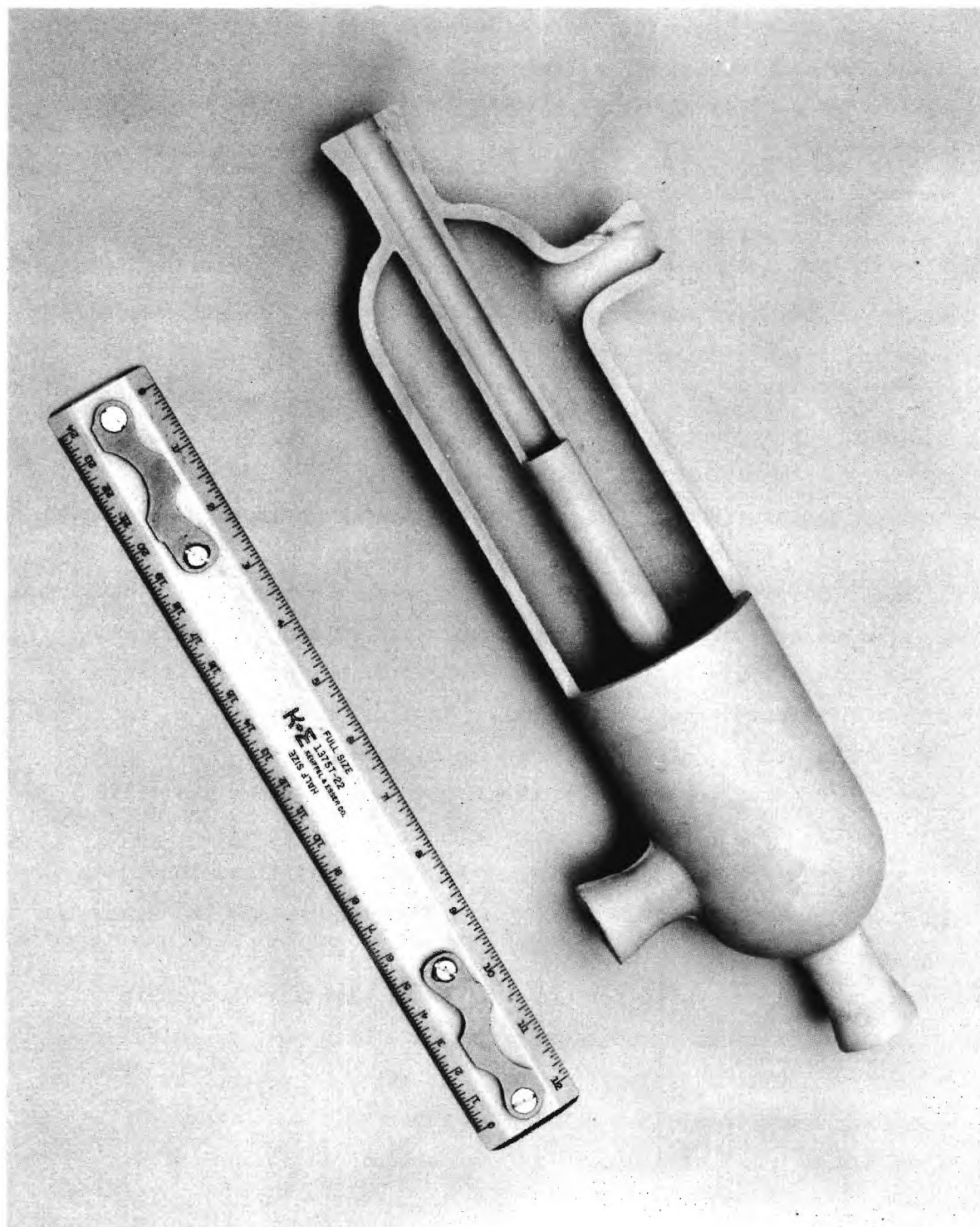


Figure 23. Slip Cast Fused Silica Heat Exchanger.

§ 3.17 Machining

Slip-cast fused silica may be machined by conventional ceramic grinding and cutting techniques. For this purpose, a bisque firing ^{1/} is often convenient followed by a second firing for development of full strength after machining.

An alternate procedure is available to permit machining with ordinary tungsten carbide tools (20). This involves impregnation of the dry, unfired casting with a resin which is burned out during the firing cycle. The strength of the fired casting is unaffected by this treatment.

§ 3.18 Surface Sealing

For use in applications involving containment of gases or liquids of low viscosity, slip-cast fused silica must be sealed. If the temperature of the sealed surface is low enough, conventional latex, phenolic, tar, or pitch sealing compounds may be used. These compounds are simply painted or troweled onto the surface and allowed to set.

In applications necessitating higher temperature seals, two methods are used to render slip-cast fused silica impermeable. In the intermediate temperature range, Teflon coatings may be used (21). A dispersion, such as du Pont No. 852-201, may be sprayed onto the silica and fused at 750° F to form a continuous coating. For higher temperature sealing, the surface of the fused silica itself may be fused by an arc-plasma jet or oxy-acetylene torch (16). This produces a dense, glassy layer with no connected pores. The arc sealing process is, of course, time consuming and tedious but the cost of slip-cast fused silica sealed by this method may still be lower than that of glass-worked fused silica in many applications. This process should be considered especially for production of shapes which are moderately complex and require a low permeability.

^{1/}See § 3.14.

§ 3.19 References for Chapter III

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NOTE: The following references are to reports issued under this contract. See Appendix B for complete listing.

24. Quarterly Report No. 2, p. 13.
25. Quarterly Report No. 3, p. 12.
26. Progress Report No. 1, p. 51.
27. Progress Report No. 2, p. 10.
28. Ibid. at p. 13.
29. Ibid. at p. 18.
30. Progress Report No. 3, p. 6.
31. Ibid. at p. 27.
32. Ibid. at p. 55.
33. Summary Report No. 2, p. 11.
34. Ibid. at p. 31.
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CHAPTER IV

PHYSICAL PROPERTIES

- § 4.1 Introduction
- § 4.2 Room Temperature Strength
- § 4.3 Elevated Temperature Strength
- § 4.4 Effects of Atmosphere on Strength
- § 4.5 Impact Strength
- § 4.6 Hardness
- § 4.7 Elastic Constants
- § 4.8 Density and Thermal Expansion Coefficient
- § 4.9 Behavior Under High Pressures
- § 4.10 Viscosity
- § 4.11 Surface Tension
- § 4.12 Vapor Pressure
- § 4.13 Gas Permeability
- § 4.14 References for Chapter IV

§ 4.1 Introduction

Many of the physical properties of fused silica depend on its microstructure. Strength, for example, is higher in transparent fused quartz than in translucent or slip-cast fused silica since the transparent material has fewer surface and internal flaws. On the other hand, many physical properties are not greatly dependent on the microstructure. All forms of fused silica, for instance, have essentially the same equilibrium coefficient of thermal expansion. In general, properties which are governed by bonding behavior depend on the microstructure and are the most favorable in transparent fused quartz. Those which are controlled only by the composition of the material will be essentially the same for all forms of fused silica.

§ 4.2 Room Temperature Strength

The strength of any given variety of fused silica will depend on the type of loading employed. Three methods are in common use, compression, tension,

and transverse rupture or bending. The tensile strength and modulus of rupture in bending are theoretically related and should be approximately equal (64). In practice, however, the tensile strength is often lower since the tensile test is more sensitive to faulty alignment of the specimen and to surface and internal flaws.

The theoretical tensile strength of fused silica can be calculated on the basis of its hypothetical structure. This strength has been estimated as 1,500,000 to 4,000,000 psi (50, 56). Strengths in this range have actually been measured in fibers of the order of one micron diameter (14, 24, 50). In one study at 78° K, tensile strengths up to 1,900,000 psi were observed in specimens from 0.43 - 0.86 mm. in diameter (34). Another showed a room temperature tensile strength of 680,000 psi in a 1-mm. diameter specimen (2, 34).

The strength of glass fibers is greatly decreased by the presence of surface defects (30, 62). Merely touching a finger tip to a fused silica fiber with a strength of 680,000 psi lowered its strength to 50,000 psi (2, 34). These surface defects can be removed by flame polishing (2) and their effects can be minimized by acid etching to round off their sharp, stress concentrating contours and to remove inclusions of foreign material (9, 10, 58, 68, 77). While there was originally thought to be a fundamental reason for the much higher strength commonly observed in fibers, evidence is available which indicates that this may occur only as a result of the lower incidence of mechanical surface damage and foreign inclusions in fibers as compared with bulk glasses (49, 53, 57, 71, 72).

The strength of bulk fused silica is strongly dependent on microstructure and the various commercial forms show different strengths. In all the forms, however, flaws and inclusions are present in large concentrations and the full strength of the material cannot be realized. In addition, the porosity in translucent and slip-cast fused silica results in a lower stress-bearing area being present than in a specimen of transparent fused silica of the same size and the apparent strength is lowered still further.

Representative values of the strength of fused silica are given in Table VII 1/.

1/See also § 3.15.

TABLE VII
ROOM TEMPERATURE STRENGTH OF BULK FUSED SILICA

	<u>Tensile</u> (psi)	<u>Compressive</u> (psi)	<u>Transverse</u> (psi)
Transparent	10,400	93,000	16,000
Translucent	3,200	44,400	6,400
Slip-Cast (Air Firing)	4,300	23,000	4,700
References: Transparent and Translucent - 39, 40 Slip-Cast - 79, Figure 11, Figure 24.			

§ 4.3 Elevated Temperature Strength

The strength of fused silica has long been known to show a substantial increase with temperature (19, 21). The reason for this increase is not clear. Stress relief by plastic flow at highly stressed points near surface flaws is possible since plastic flow under deformation has been demonstrated even at room temperature (1, 59). Since the strength increases essentially constantly as the temperature is increased, while the viscosity shows a very slow change ^{1/}, this is unlikely to be a predominant mechanism. An unexplained molecular rearrangement has also been suggested (20). One mechanism, which has been fairly clearly demonstrated, is that surface flaws, resulting from thermal shock of the cristobalite formed during fabrication, become filled in as the cristobalite expands on heating. As these flaws are filled by the expanding cristobalite, they become more mechanically stable and tend to act less as stress concentrators (15).

The tensile strength of fused silica is shown as a function of temperature in Figures 24 (80) and 25 (40, 80).

§ 4.4 Effects of Atmosphere on Strength

Exposure to different atmospheres can affect the strength of fused silica both through alteration of the surface energy conditions and through

^{1/}See § 4.10.

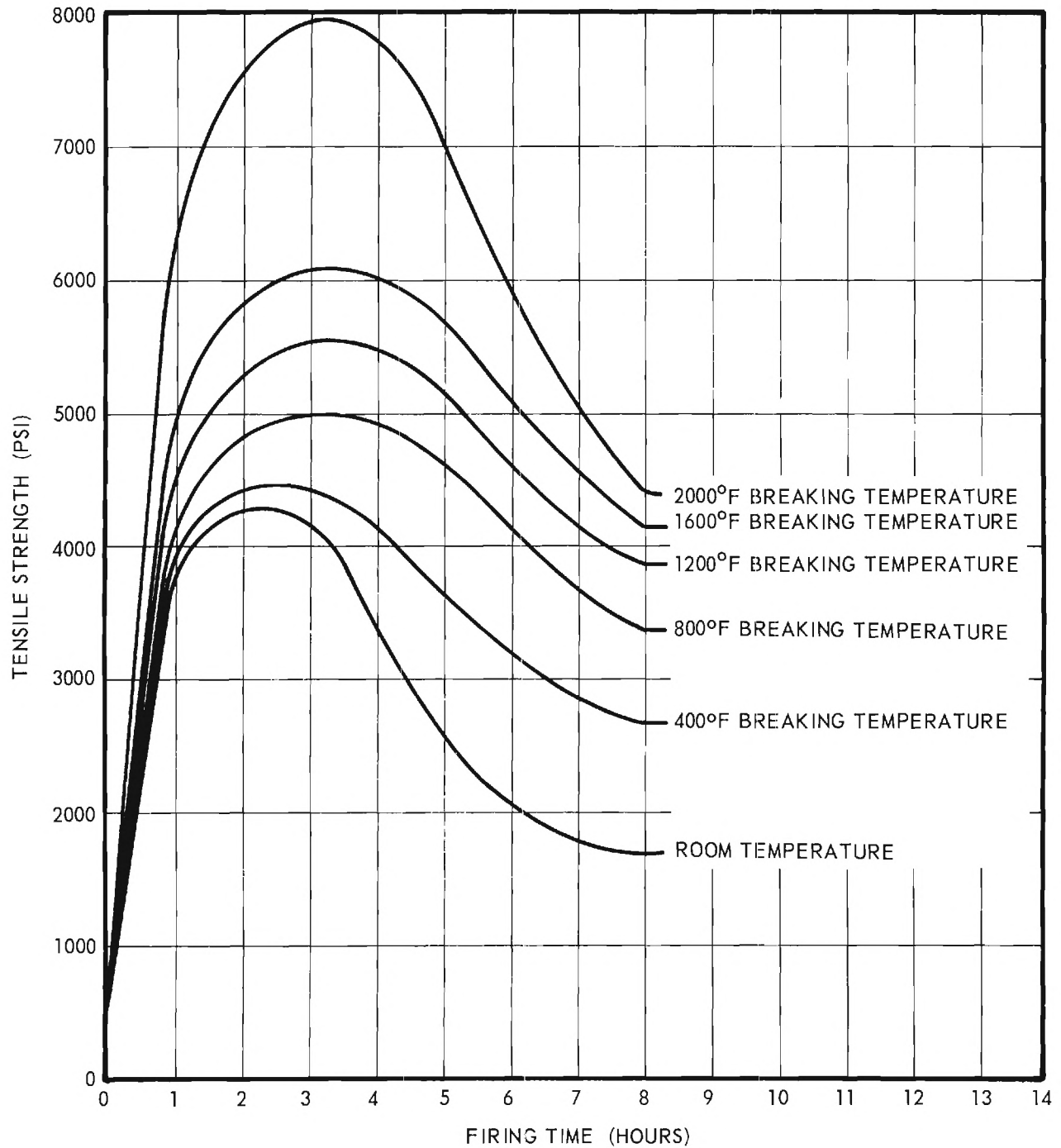


Figure 24. Elevated Temperature Tensile Strength of Slip Cast Fused Silica Fired at 2200°F.

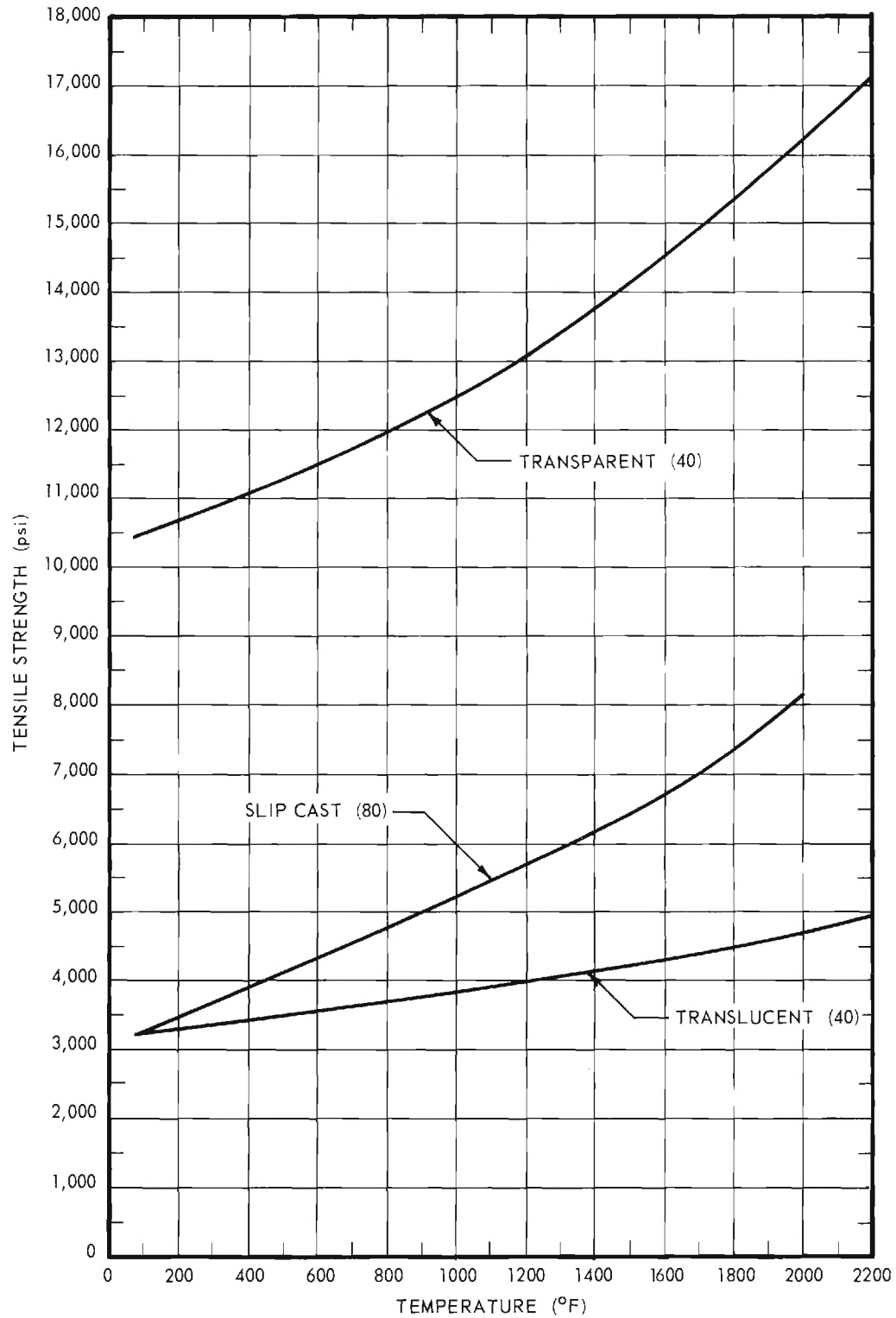


Figure 25. Elevated Temperature Tensile Strength of Fused Silica.

chemical attack by the atmosphere. The two effects are similar in some ways but they differ fundamentally.

Fused silica shows a decreased strength after a very short exposure to various vapors. Hammond and Ravitz found a correlation between the fracture stress of fused silica and the lowering of the surface free energy of quartz by the environmental vapor (31). The tensile strength of fused silica fibers decreased from 13,200 psi in a vacuum to 6,600 psi in water vapor. Vapors of lower polarity than water produced intermediate strengths. Hammond and Ravitz explained these results as being due to the fracture of highly strained Si-O-Si bonds at the tips of surface flaws, as postulated by Hynd (35) and Weyl (75). This effect is distinguished from the similar effects of corrosion by the fact that the strength does not decrease in a consistent manner with increasing water vapor pressure, but instead a bimodal relationship is observed (61).

If fused silica is exposed for a longer time, the atmosphere can produce new flaws and increase the effects of those already present. This chemical attack produces different results depending on whether the silica is stressed or not. Under stress, the chemical activity at the roots of the surface flaws is greatly increased and atmospheric attack selectively extends the flaws, resulting in earlier failure (5). If the specimen is not stressed, atmospheric attack tends to round the flaws and, under subsequent stressing, the strength is increased rather than decreased ^{1/}. Under stress, the attack can be quite rapid at elevated temperatures. Charles found that the compressive strength of fused silica in dry nitrogen was 64,500 psi while exposure to water vapor at room temperature lowered the strength to 55,600 psi and, at 460° F, to 36,600 psi (17).

§ 4.5 Impact Strength

Moore determined the impact stress required to produce fracture in a cube exposed to a falling weight (48). The impact stress required to

^{1/}See § 4.2.

fracture transparent fused silica was 12,100 psi compared with 11,700 for translucent fused silica. In the same apparatus, alumina gave an impact fracture stress of 43,400 psi.

Kurlyankin and Konovalova determined the impact strength in beam loading using a falling pendulum, apparently as in a Charpy test (40). Transparent and translucent fused silica were tested up to 2200° F. The results are shown in Figure 26.

No measurements have been made of the impact strength of slip-cast fused silica. Since the impact strength is dependent on the porosity, slip-cast fused silica will be lower in strength than transparent fused silica and possibly slightly lower than translucent.

§ 4.6 Hardness

The hardness of fused silica as a function of temperature has been determined by Westbrook (74). As shown by Mackenzie, the hardness in the range of 900° to 1100° F shows a dependence on the thermal history (43) 1/. The variation of hardness with temperature is shown in Figure 27.

§ 4.7 Elastic Constants

Several dynamic measurements of the elastic constants of fused silica have been reported in recent years (47, 65, 66). Figures 28 and 29 show the variation of Young's and shear modulus and Poisson ratio with temperature according to Spinner's results (67).

The dynamic modulus of slip-cast fused silica has not been measured. A rough static measurement showed the room temperature Young's modulus to be 3.75×10^6 psi (78) 2/.

§ 4.8 Density and Thermal Expansion Coefficient

As mentioned previously 3/, the density and thermal expansion coefficient of fused silica depend on its equilibrium temperature. Douglas and Isard showed that fused silica has a negative thermal expansion coefficient in the

1/See § 2.9.

2/After completion of this report, data were received from Mr. Carlyle F. Smith, Pfaudler Co. (Division of Pfaudler Permutit, Inc.) from sonic measurements on slip-cast silica, including foam. While space does not permit this information to be given in the detail it deserves, the data may be represented approximately by

$$\log_{10} \text{ Young's Modulus (psi)} = 5.068 + 0.0124 \rho \text{ (lb/ft}^3\text{)}$$

$$\log_{10} \text{ Shear Modulus (psi)} = 4.658 + 0.0130 \rho \text{ (lb/ft}^3\text{)}.$$

3/See § 2.19.

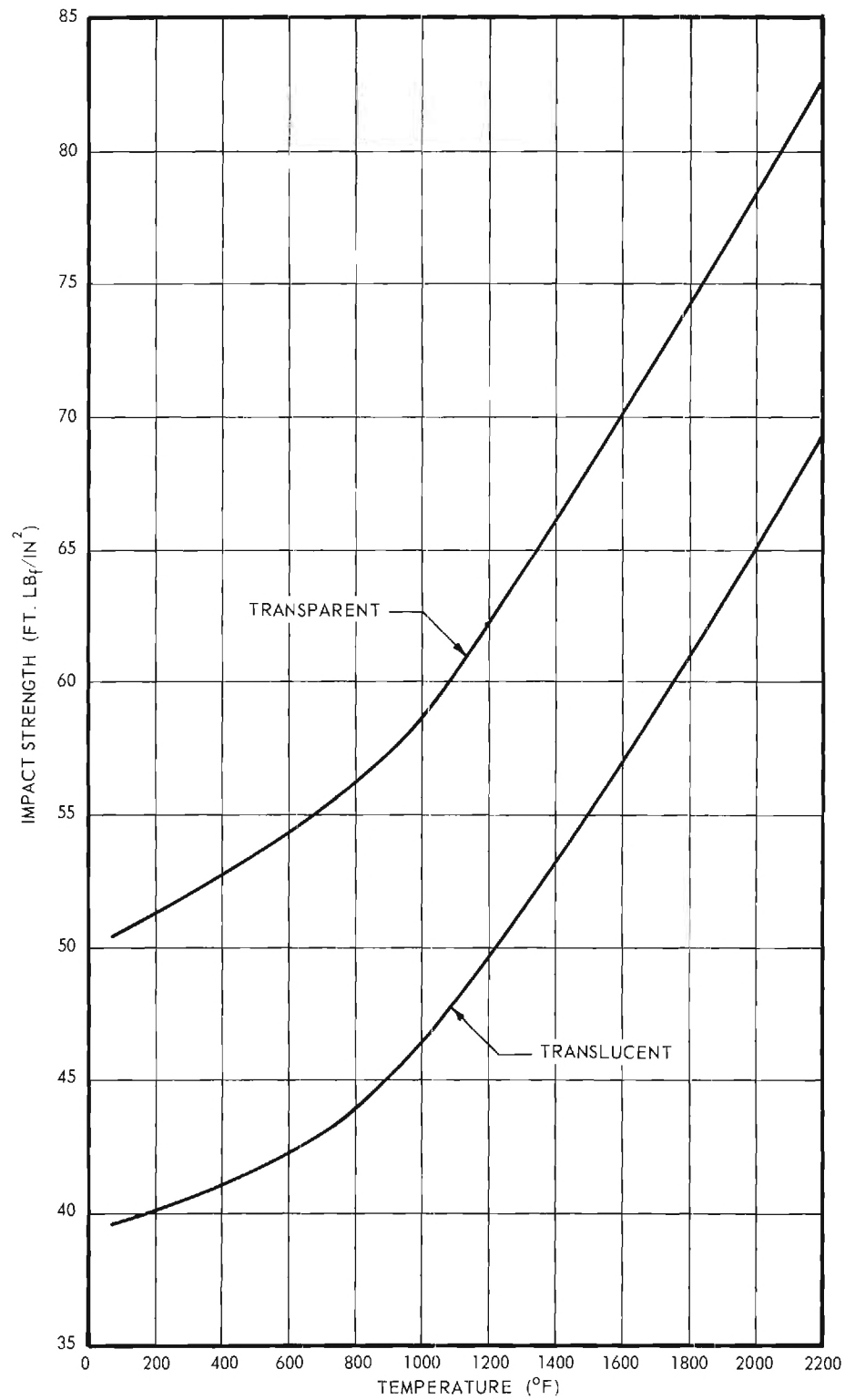


Figure 26. Impact Strength of Fused Silica.

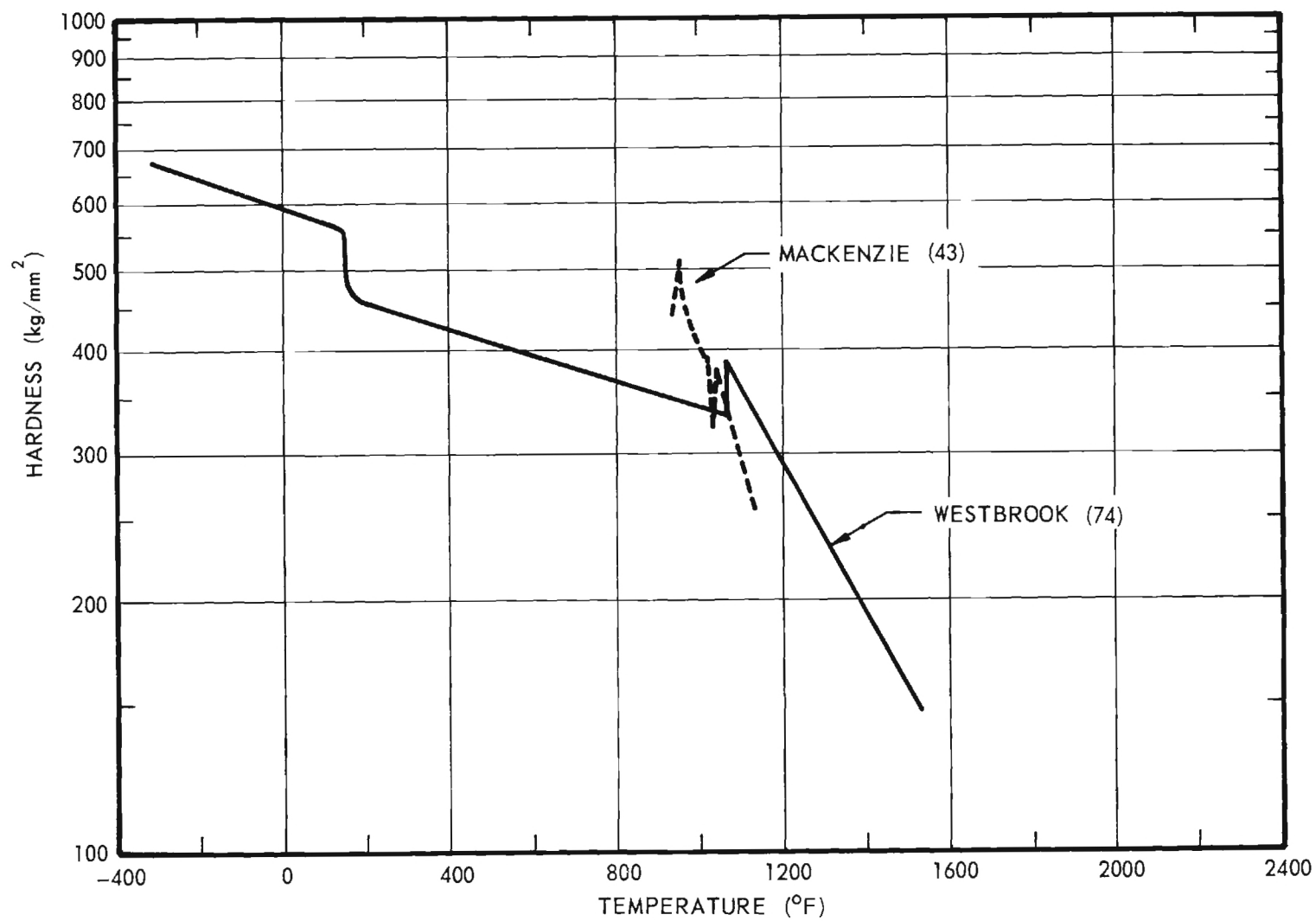


Figure 27. Hardness of Transparent Fused Silica.

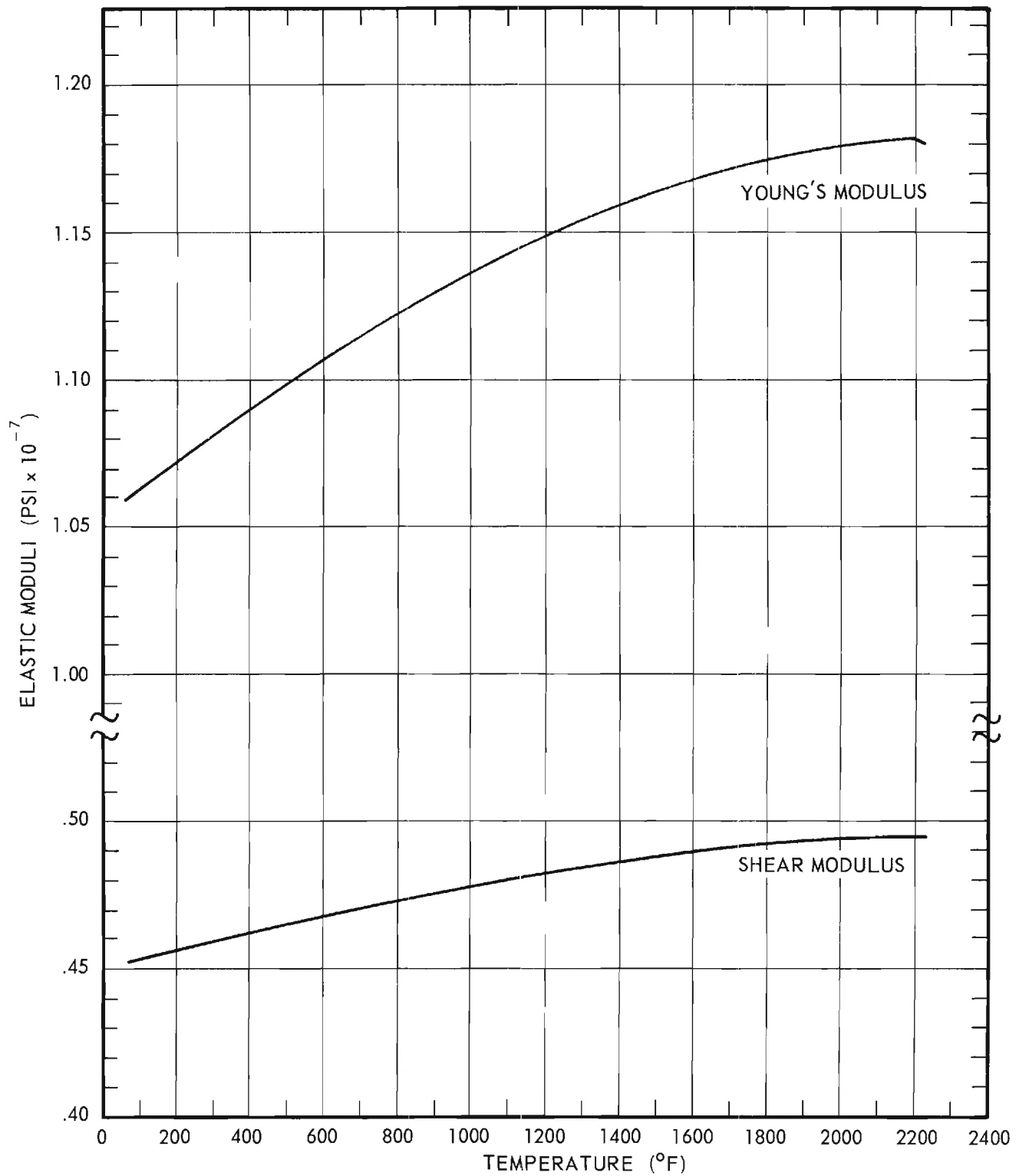


Figure 28. Young's Modulus and Shear Modulus of Transparent Fused Silica.

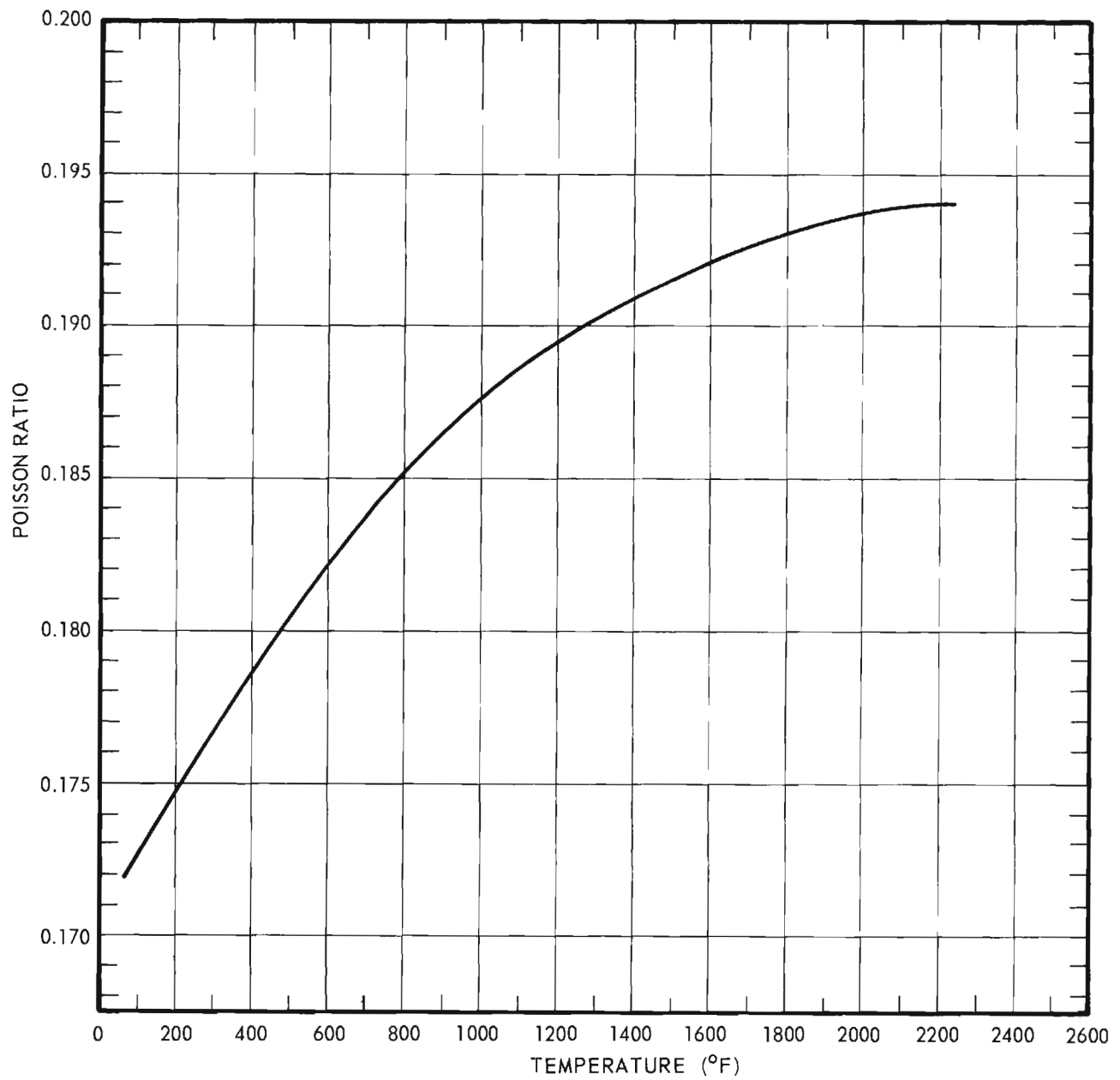


Figure 29. Poisson Ratio of Transparent Fused Silica.

temperature range above about 1800° F if it is allowed to reach equilibrium at each temperature (23). Brückner verified these results and found further that fused silica shows a normal positive thermal expansion coefficient if the temperature is changed too rapidly to permit equilibration (13). Brückner proved that, above about 200° F, the thermal expansion coefficient increases with increasing equilibrium temperature up to an equilibrium temperature of about 2700° F, above which the trend reverses. Below about 200° F, the thermal expansion coefficient decreases with increasing equilibrium temperature up to an equilibrium temperature of about 3150° F and then begins to increase again. These results are summarized in Figures 30 and 31 1/.

The lines of negative slope in Figure 30 show the density variation with ambient temperature and equilibrium temperature. The line marked "Equilibrium Curve" shows the density of fused silica heated slowly enough to equilibrate at each temperature.

In Figure 31, the solid lines represent the extreme limits of thermal expansion coefficients which Brückner determined in samples with different known equilibrium temperatures. These curves show that different investigators can be expected to obtain rather divergent values of the thermal expansion coefficient, even aside from intrinsic errors in their techniques, if the samples are studied without a known, standard annealing operation. Since the need for this standard anneal has not been widely appreciated, the values in the literature do differ somewhat. Values from the recent literature are shown in Figure 31. It is obvious that these values may all be of equal accuracy and that the differences may have arisen simply from the use of samples having different equilibrium temperatures. Since the thermal expansion coefficients vary over a reasonably wide range, selection of a valid "average" coefficient is evidently impossible. The thermal expansion coefficient is quite small regardless of the equilibrium temperature, and the differences may ordinarily be unimportant. In some cases, however, the differences may be critical. In an analysis of thermal shock, for example, the stress could be different by a factor of two or more for different equilibrium temperatures.

While a practical structural application probably cannot be analyzed

1/See § 3.15 for density of slip-cast fused silica.

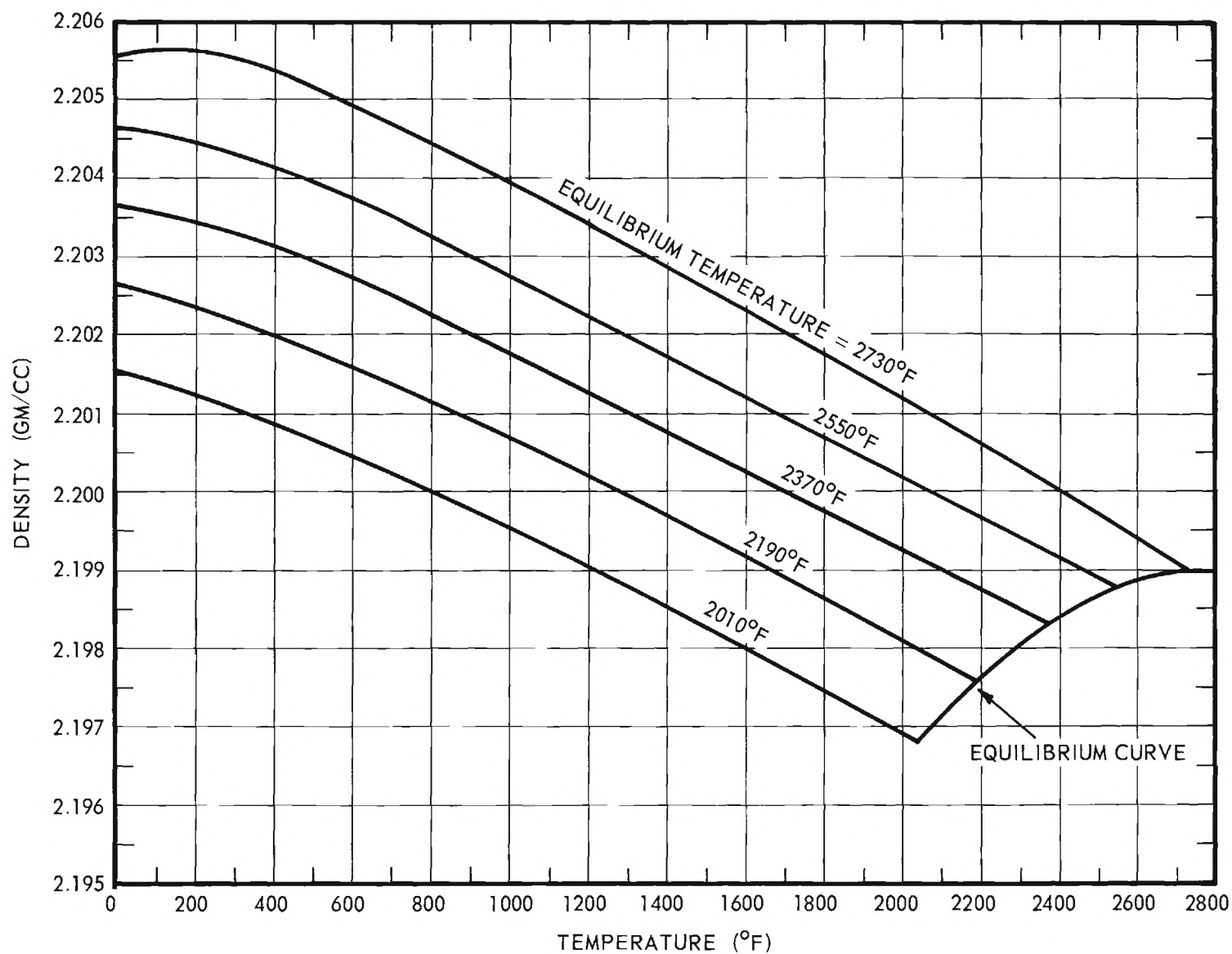


Figure 30. Theoretical Density of Fused Silica as a Function of Equilibrium Temperature.

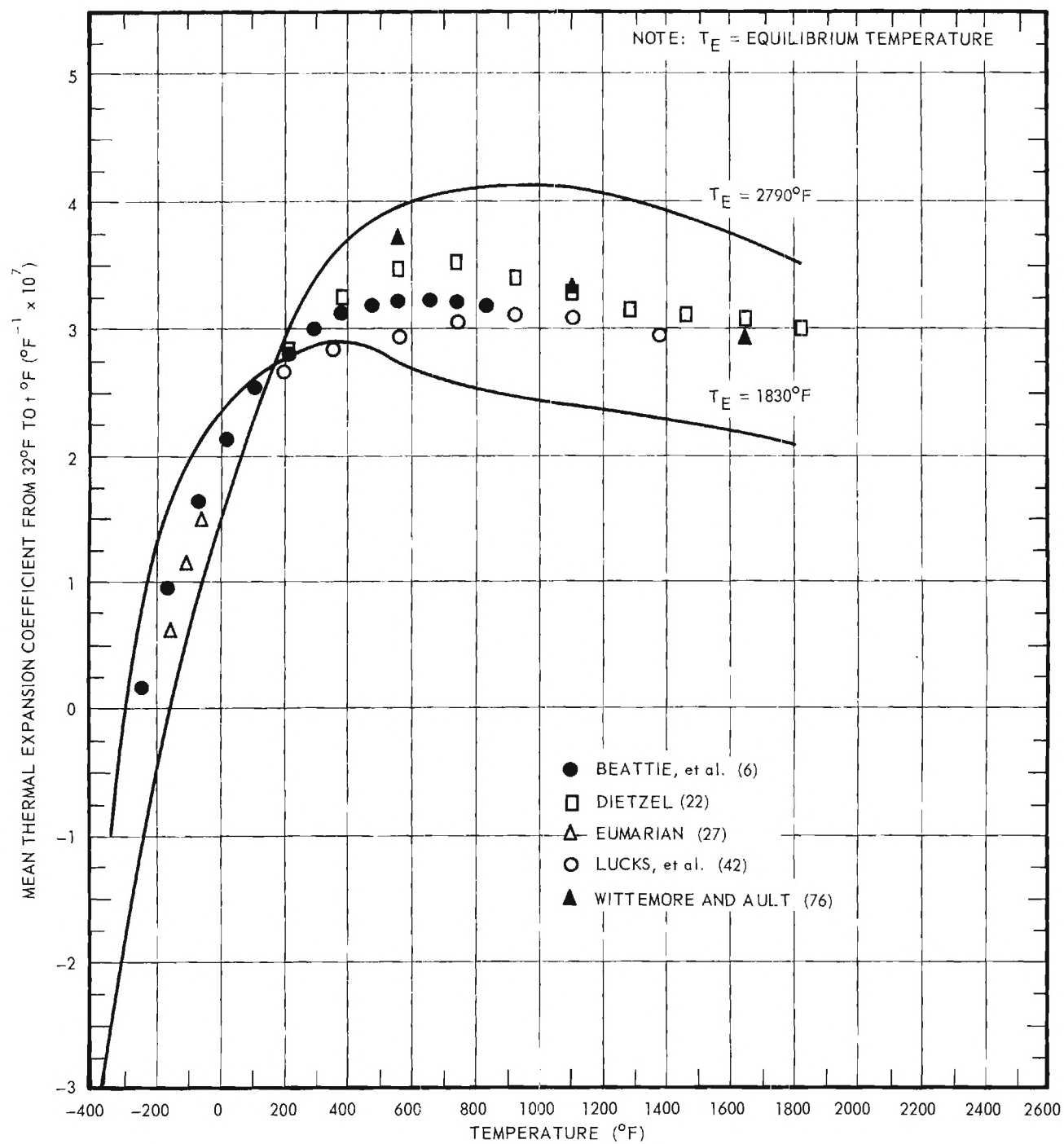


Figure 31. Theoretical Expansion Coefficient of Fused Silica.

with sufficient precision to permit exact specification of a thermal expansion coefficient, further consideration of the problem may serve to indicate approaches which will be useful in particular cases.

The time required for a specimen to equilibrate at a given temperature does not vary strongly with its previous equilibrium temperature since the rate of equilibration is roughly exponential with time. For example, Douglas and Isard found that a specimen with an equilibrium temperature of about 2230° F required essentially the same time to equilibrate at 1980° F as one with an equilibrium temperature of about 1830° F, although the curves of density versus time were quite different (23). As a result, although without a theoretical basis, a plot of time to equilibrate as a function of temperature may be drawn as a guide. Such a plot, drawn from the data of Douglas and Isard, is given in Figure 32. It should be remembered that this figure is to be used as a guide only since it is of uncertain theoretical validity and is based on scanty data. Figure 32 shows that equilibrium is attained in a reasonably short time at temperatures above about 2200° F and that equilibration at temperatures below about 1900° F requires an extremely long time. In view of these conclusions, a safe assumption seems to be that normal air cooling will produce a rate of temperature change such that glass-worked fused silica will have an equilibrium temperature of perhaps 2300° to 2500° F. The one hour anneal at approximately 1920° F, which is usually applied in glass-working, is not of sufficient duration to affect this equilibrium temperature. Slip-cast fused silica is fired for approximately four hours at 2200° F ^{1/}. Since this exceeds the equilibration time at 2200° F and since the slip-cast silica is air cooled after firing, its equilibrium temperature should be 2200° F, lower than that of glass-worked fused silica.

Reference to the data points in Figure 31 shows that their position is consistent generally with an equilibrium temperature of about 2300° to 2500° F as would be expected since the specimens represented are glass-worked fused silica. Slip-cast fused silica might then be expected to fall slightly below these points.

^{1/}See § 3.14.

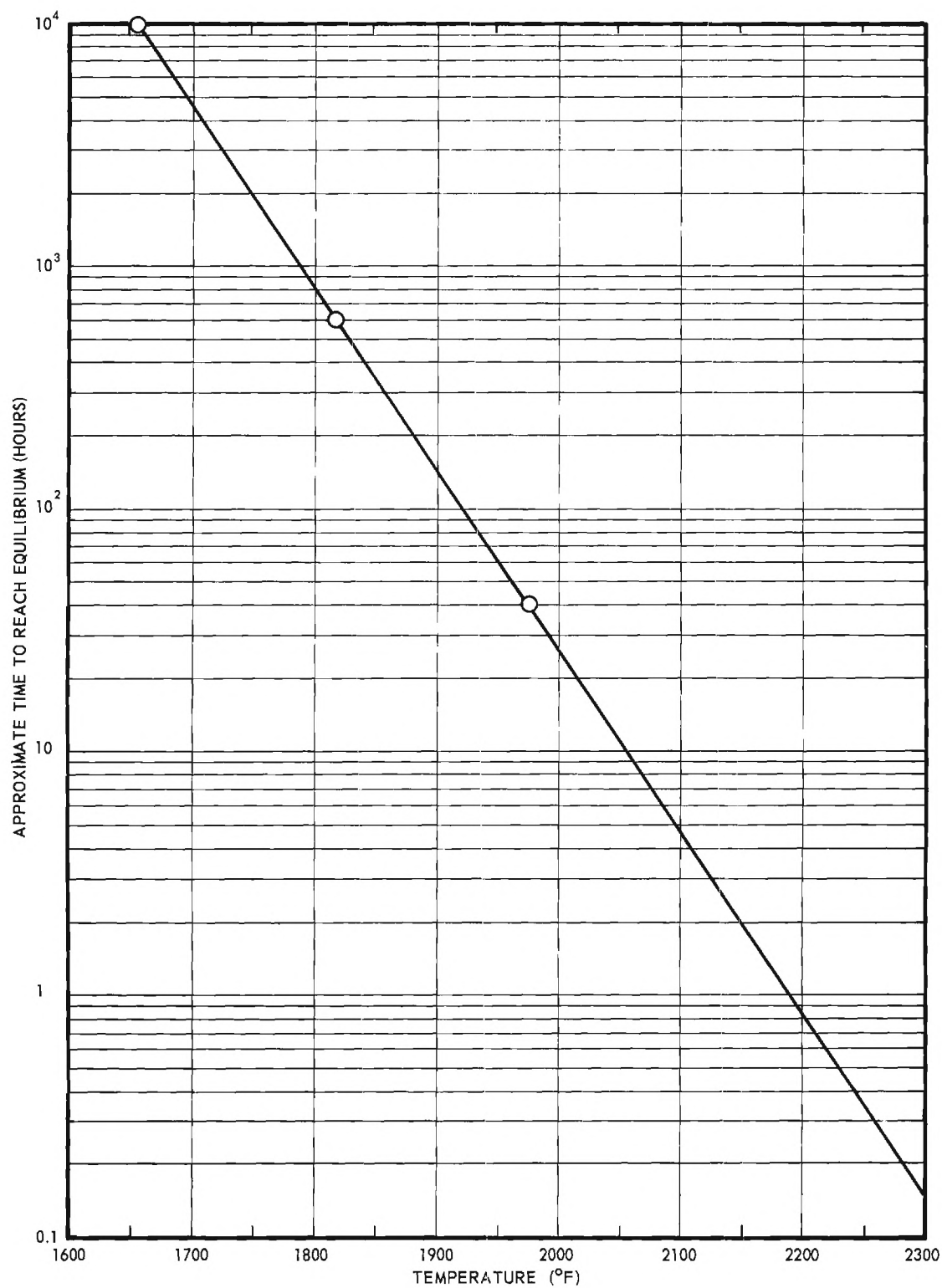


Figure 32. Approximate Time to Reach Equilibrium Density as a Function of Temperature.

Attention should be given to the fact that the thermal expansion coefficient will probably alter in normal structural applications. For example, consider fused silica with an equilibrium temperature of 2400°F which is to be used as a structural part at an ambient temperature of 2000°F . Reference to Figure 30 shows that the silica has a room temperature theoretical density of about 2.2038 gm/cc . On heating to 2000°F , little equilibration occurs since the heating time is probably much less than the 26 hours which Figure 32 shows to be necessary for equilibration at a constant temperature of 2000°F . The specimen thus expands with a thermal expansion coefficient probably falling within the data points in Figure 31, and with a density which decreases along a line parallel to the 2370°F equilibrium temperature line in Figure 30. The terminal density at 2000°F is about 2.1994 gm/cc . As the specimen soaks at 2000°F , it adjusts to the new equilibrium temperature of 2000°F , expanding still further over a period of about 26 hours to a density of about 2.1968 gm/cc . Now, on cooling, the specimen will parallel the 2010°F equilibrium temperature curve, arriving at room temperature with a density of about 2.2013 gm/cc and a thermal expansion coefficient which should fall between the data points and the 1830°F equilibrium temperature line in Figure 31.

Hetherington and Jack found that the density and thermal expansion coefficient of fused silica decrease and increase respectively with increasing water content (33) ^{1/}. The values for specimens of electrically fused, flame fused, and synthetic fused silica of the same equilibrium temperature are given in Table VIII. Upon heating in a given atmosphere, the water content tends to approach an equilibrium value so that these properties would ultimately become the same regardless of initial water content. Since the diffusion of water is geometry controlled, however, a longer time may be required to attain the equilibrium water content than to reach the equilibrium temperature (7).

^{1/}See § 2.13.

TABLE VIII

DENSITY AND THERMAL EXPANSION COEFFICIENT
OF TRANSPARENT FUSED SILICA WITH DIFFERENT WATER CONTENT*

Type	Water Content (w/o - OH)	Density (gm/cc)	Average Thermal Expansion Coefficient (32-212° F) (°F ⁻¹ x 10 ⁷)
Electrically Fused	0.0003	2.203	2.67
Flame Fused	0.040	2.201	----
Synthetic	0.125	2.197	2.89

* Equilibrium Temperature \pm 1900° F.

The preceeding discussion shows that:

1. Fused silica specimens from different manufacturing cycles are initially likely to show somewhat different densities and thermal expansion coefficients.
2. Any type of fused silica will tend to approach the same density and thermal expansion coefficient in service at a given temperature.
3. For applications involving rapid heating, the thermal shock resistance should be improved by low temperature annealing and low water content.

§ 4.9 Behavior Under High Pressures

While the behavior of fused silica at high pressures is not likely to be of concern in structural applications, it is interesting enough to deserve a brief mention. Unlike most other inorganic solids, fused silica and other glasses remain compressed after the application of high pressures until the densification is relieved by annealing (12, 18). The density of fused silica is increased by about 18 per cent after application of 80,000 atmospheres, it becomes much stronger, and a new structure results which is insoluble in

hydrofluoric acid (38).

The elastic compressibility of fused silica is quite reproducible at low pressures. At one atmosphere, this compressibility has been determined to be $9.9 \times 10^{-7} \text{ atm.}^{-1}$ (25). As the pressure is increased to the point of substantial volume decrease, however, the nature of the compression becomes very much more complex. Mackenzie found that the amount of densification increased not only with time, temperature, and pressure, as would be expected, but also quite substantially with the extent of applied shear (45). As a result, the compressibility of fused silica at higher pressures cannot be expressed as a simple function of the ambient conditions.

The compression of fused silica does not alter the basic arrangement of the silica tetrahedra (12). The mechanism has been explained in terms of bending the Si-O-Si bonds (63) but Mackenzie concluded that the strong dependence on the applied shear implies that units of the random silica chain are caused to interlock under the combined pressure and shear so that the structure becomes less open (45). This model is consistent with the relief of the densification which Mackenzie found to occur upon heating (46).

§ 4.10 Viscosity

Bacon, et al (3, 4) and Hasapis, et al (32) have measured the viscosity of fused silica up to 4200° F. By combining their data with that available in the literature for lower temperatures, Bacon concluded that fused silica follows an Arrhenius equation over the range 2800° to 4500° F (4). Mackenzie, however, pointed out that this behavior is most unusual for associated liquids and that the fused silica structure as commonly pictured necessitates a high degree of association (44). Mackenzie applied a statistical analysis to the data which Bacon used in support of the Arrhenius behavior and determined that there is indeed substantial deviation from such behavior. The viscosity data from Mackenzie's recalculation are combined with lower temperature data in Figure 33.

Isard and Douglas showed that the viscosity of fused silica is affected by its equilibrium temperature and determined the viscosity of a fused silica sample, with an initial equilibrium temperature above the ambient temperature, both before and after equilibration (36). These points are included in Figure 33.

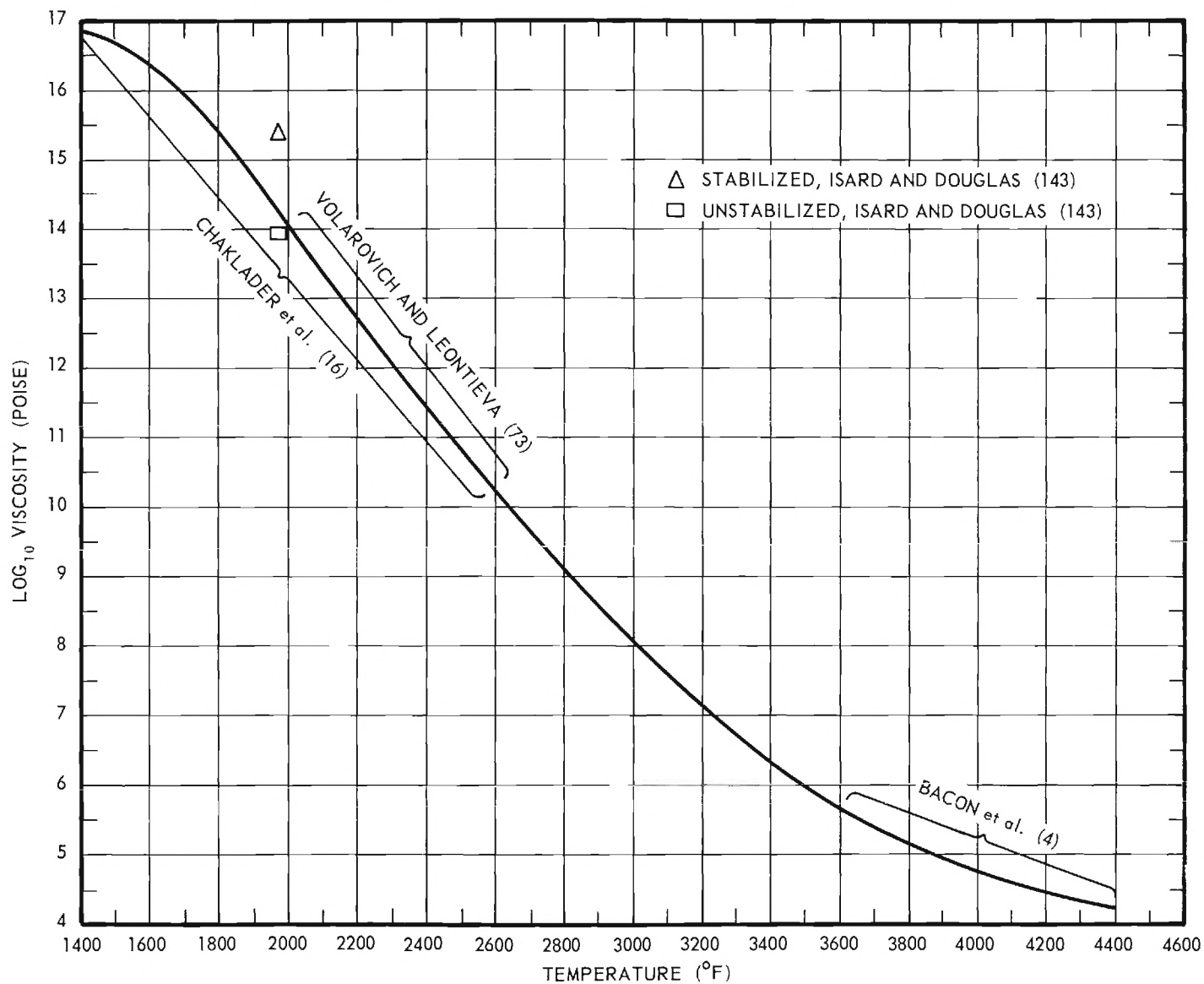


Figure 33. Viscosity of Fused Silica.

This indicates that the creep strength of fused silica might be higher in a sample of low equilibrium temperature. Since equilibration is rapid at any temperature at which creep is significant, however, this is of little importance. In the same manner, the lower viscosity associated with a higher equilibrium temperature might also promote sintering but rapid equilibration in the sintering temperature range also renders this effect minimal.

Hetherington and Jack demonstrated a decrease in the viscosity of fused silica with increasing water content (33) 1/. The viscosity of electrically fused silica was approximately half an order of magnitude greater than that of flame fused silica and approximately an order of magnitude greater than that of synthetic fused silica. These viscosity differences should produce differences in creep strength and sintering rate similar to those mentioned above in connection with the equilibrium temperature. The effects of water content should be more lasting, however, in view of the greater time required for equilibration. This effect undoubtedly accounts for the great increase in the sintering rate noted in steam sintering slip-cast fused silica 2/.

§ 4.11 Surface Tension

Norton and Kingery (51), Parikh (54), and Kingery (37) have measured the surface tension of fused silica. Their results are shown in Figure 34.

Kingery found that fused silica shows a positive temperature coefficient of surface tension as opposed to salts, water, metals, and organic liquids (37). He interpreted this observation as indicating a significant degree of alteration in the association of fused silica above its melting point.

§ 4.12 Vapor Pressure

Silica does not vaporize in a simple equi-molecular process. Brewer and Mastick interpreted thermochemical data to show that SiO is the principal vaporizing species under neutral conditions (11). Porter, et al, carried out a mass spectrometric search to determine the products of the vaporization process (55). They detected SiO, SiO₂, Si₂O₂, O₂, and O, indicating that

1/See § 2.13.

2/See § 3.15.

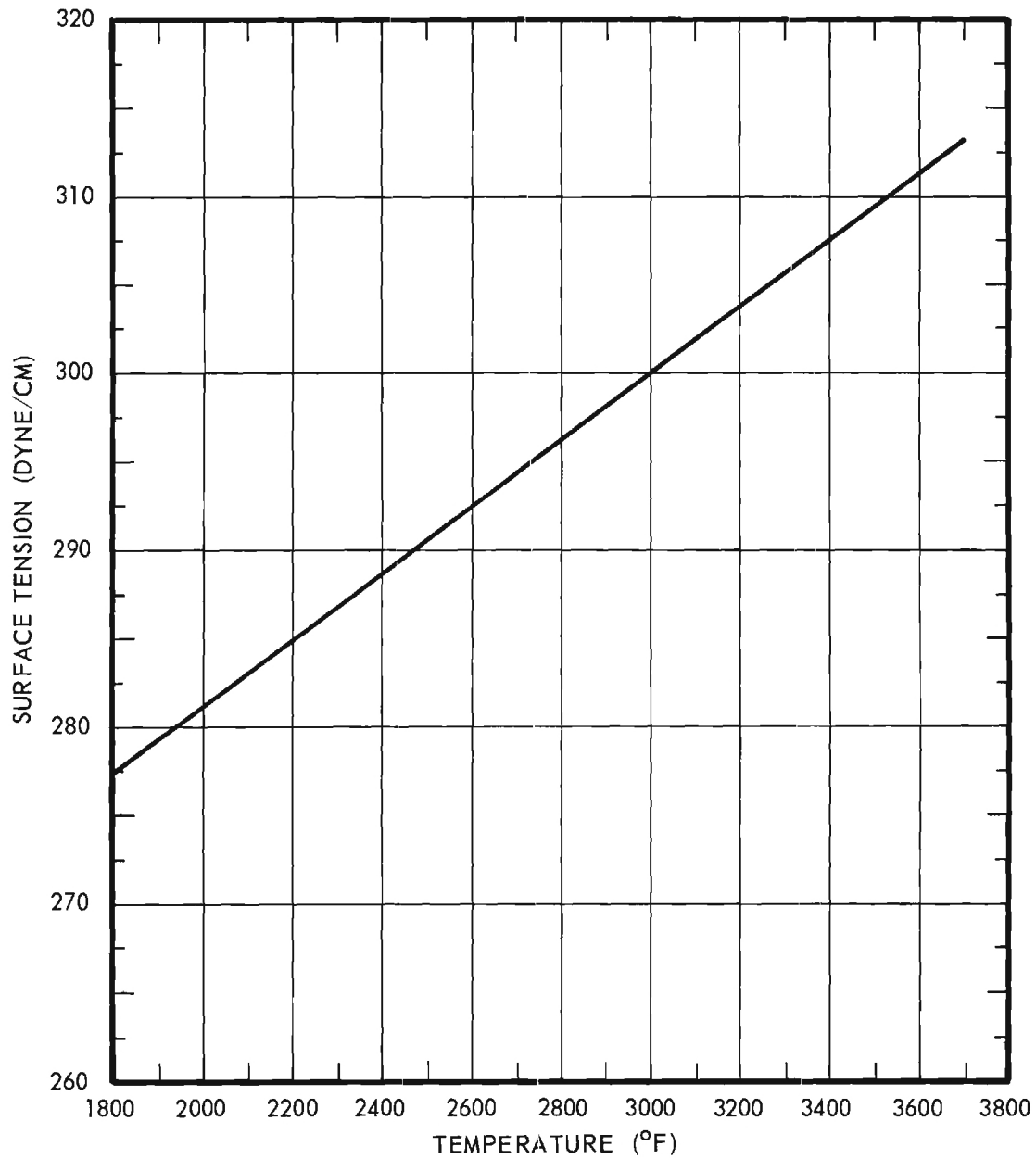
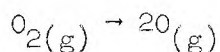
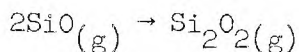
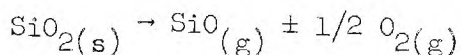
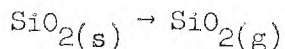


Figure 34. Surface Tension of Fused Silica.

the following reactions occur during vaporization:



Schick applied an excellent and extensive thermochemical analysis to these reactions in neutral, oxidizing, and reducing atmospheres (60). His results confirmed the experimental findings of Brewer and Mastick (11) and of Porter, et al (55). Schick's results for neutral conditions and air at one atmosphere are given in Figures 35 and 36. The original article includes data for several other conditions.

§ 4.13 Gas Permeability

Fused silica shows a low permeability for all gases except those of low molecular weight at high temperatures. Even then, fused silica is often less permeable than metals (26). Since the porosity of translucent fused silica is closed, transparent and translucent fused silica should not differ markedly. Since the porosity of slip-cast fused silica is open, however, high permeability results (28) and slip-cast fused silica should not be considered for gas retention applications except in special instances in which surface sealing is permissible 1/ or a relatively high permeation rate is not objectionable. The permeation rate of air through slip-cast fused silica is approximately 0.017 lb/ft² hr. psi/in. at room temperature.

When stressed, fused silica becomes slightly more permeable to gases. Under a stress of 5000 psi, for example, fused silica was found to increase in hydrogen permeability by one per cent (69).

The rate of surface adsorption may be important in controlling gas permeation through thin sections of fused silica. Börnert and Von Weber, for example, found a substantial increase in the permeation of hydrogen

1/See § 3.18.

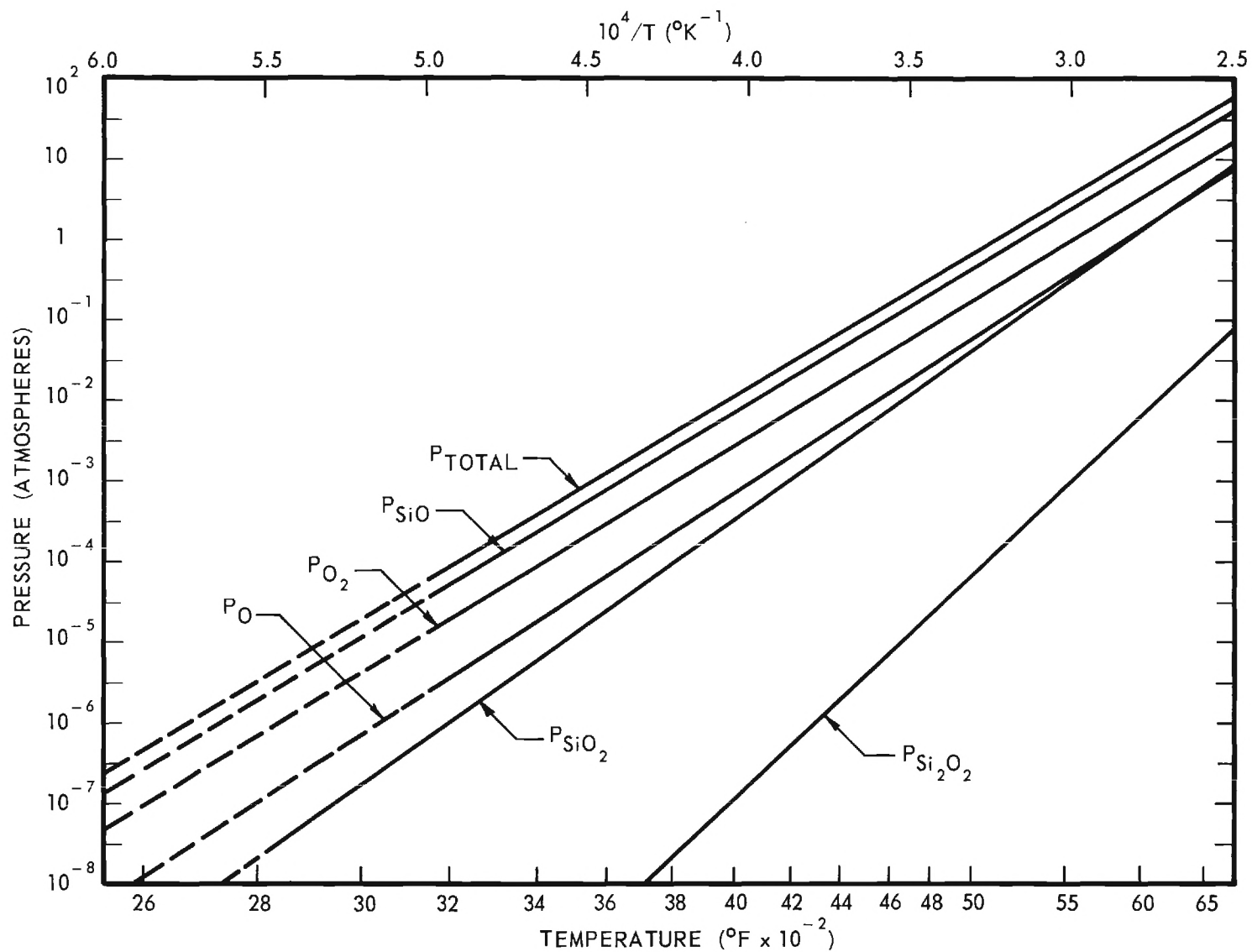


Figure 35. Vapor Pressure of Fused Silica in a Neutral Atmosphere.

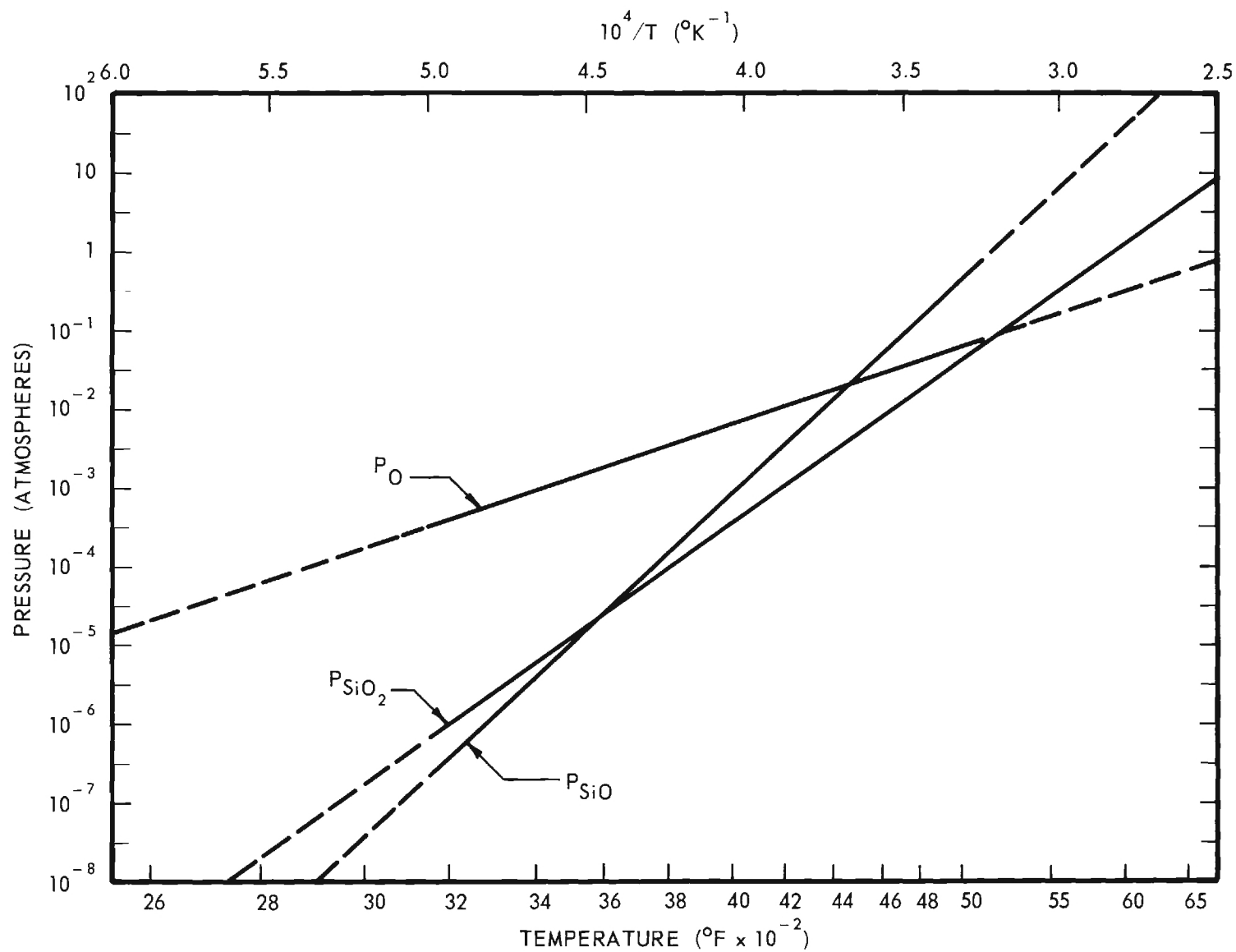


Figure 36. Vapor Pressure of Fused Silica in Air at a Total Pressure of One Atmosphere.

through fused silica when its surface was coated with palladium (8).

Diffusion rates of several gases through transparent fused silica are shown as a function of temperature in Figure 37.

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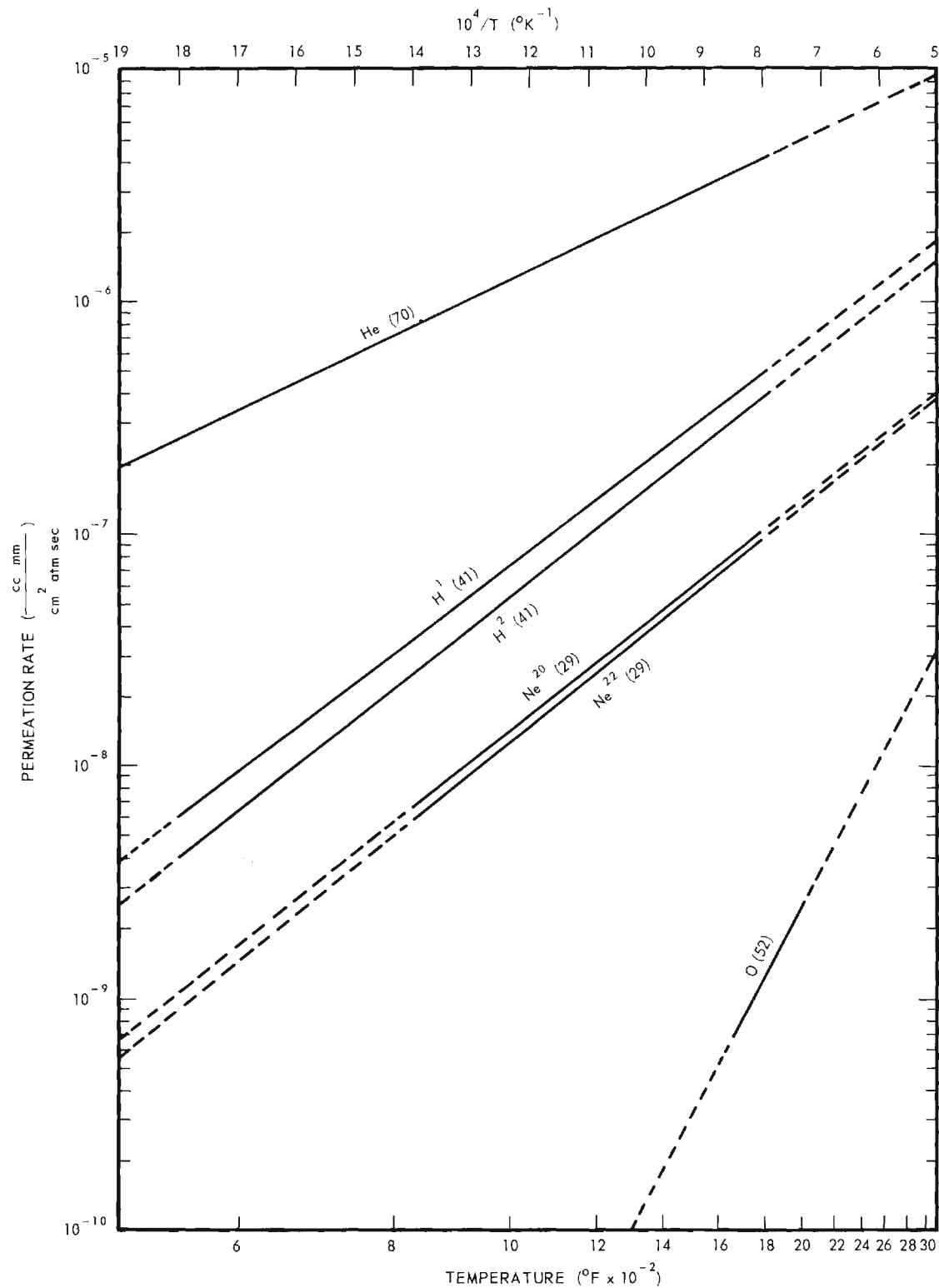


Figure 37. Permeation Rates of Various Gases Through Fused Silica.

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NOTE: The following references are to reports issued under this contract.
See Appendix B for complete listing.

78. Progress Report No. 3, p. 110.
79. Summary Report No. 2, p. 10.
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CHAPTER V

THERMOPHYSICAL AND THERMOCHEMICAL PROPERTIES

- § 5.1 Thermal Conductivity
- § 5.2 Emissivity
- § 5.3 Heat Capacity
- § 5.4 Enthalpy
- § 5.5 Heat and Free Energy of Formation
- § 5.6 References for Chapter V

§ 5.1 Thermal Conductivity

The thermal conductivity of fused silica is structure dependent. Since slip-cast fused silica is porous, it contains numerous air pockets which are small enough not to be subject to internal convection currents but numerous enough to have a significant effect in lowering the conductivity. As a result, the thermal conductivity of slip-cast fused silica is somewhat lower than that of glass-worked fused silica at moderate temperatures. Although translucent fused silica also contains gas pockets, the void fraction is not sufficiently high to have much influence on thermal conductivity and both transparent and translucent fused silica have about the same thermal conductivity up to approximately 750° F (9).

At approximately 900 to 1000° F, radiation becomes important in determining the effective thermal conductivity of transparent fused silica since its transmittance in the infrared region is good (13). As a result, if the transparent fused silica separates hot and cold surfaces, direct radiation through the specimen constitutes a significant part of the total heat transfer. Kingery, for example, found that at about 1830° F, heat transfer by radiation and conduction through a transparent fused silica specimen were approximately equal (11). Care must obviously be taken in distinguishing between total conductivity, including radiation, and true conductivity in making heat transfer calculations for transparent fused silica.

Slip-cast fused silica shows much different behavior in the high temperature region. Its porosity produces vast numbers of internal reflecting surfaces and radiation contributes essentially nothing to its conductivity.

As a result, in the temperature region above about 1800° F, slip-cast fused silica can be expected to transfer less than half the heat transferred through an equal thickness of transparent fused silica and the difference will increase rapidly with temperature.

To a much smaller extent, translucent fused silica also shows a lower total conductivity at elevated temperatures than transparent fused silica since its internal porosity does decrease radiant energy transfer. This effect has not been quantitatively determined, but will probably bring the total conductivity closer to that of slip-cast fused silica than to that of transparent fused silica.

Direct radiation through fused silica has made determination of its true thermal conductivity difficult. While the measurements of recent investigators are in reasonable agreement in the low temperature region, substantially different results have been obtained in studies above about 1800° F. This is apparent from the curves of Figure 38. Curve A represents the data obtained by Lucks, et al, in an experiment without precautions against direct radiation (13). Curve B represents Lucks' data obtained with the same specimen but with protection against direct radiation. Curve C is an average composite of data. Below 1500° F, the data were drawn from Berman (3), Kingery (11), Ratcliffe (15), and Devyatkova, et al (5) whose results showed good agreement. Above 1500° F, the data for Curve C were drawn only from Devyatkova, et al. Curve D was taken from Wray and Connolly (19).

Several interesting features are seen in Figure 38. Although Devyatkova applied a correction for direct radiation, the high temperature results are seen to parallel the results of Lucks obtained without radiation shields. On the other hand, Lucks' results obtained with a radiation shield parallel those of Wray and Connolly obtained using a technique which the authors felt to be free of significant radiation effects. The obvious conclusion is that the high temperature results of Devyatkova are not free of direct radiation. Since the lower end of Curve C is drawn from the data of four investigators, it probably is most accurate. This curve can be blended with Curve D, as shown by the dashed line, to form a single curve which appears at the present time to be the best representation of the thermal conductivity of transparent fused silica.

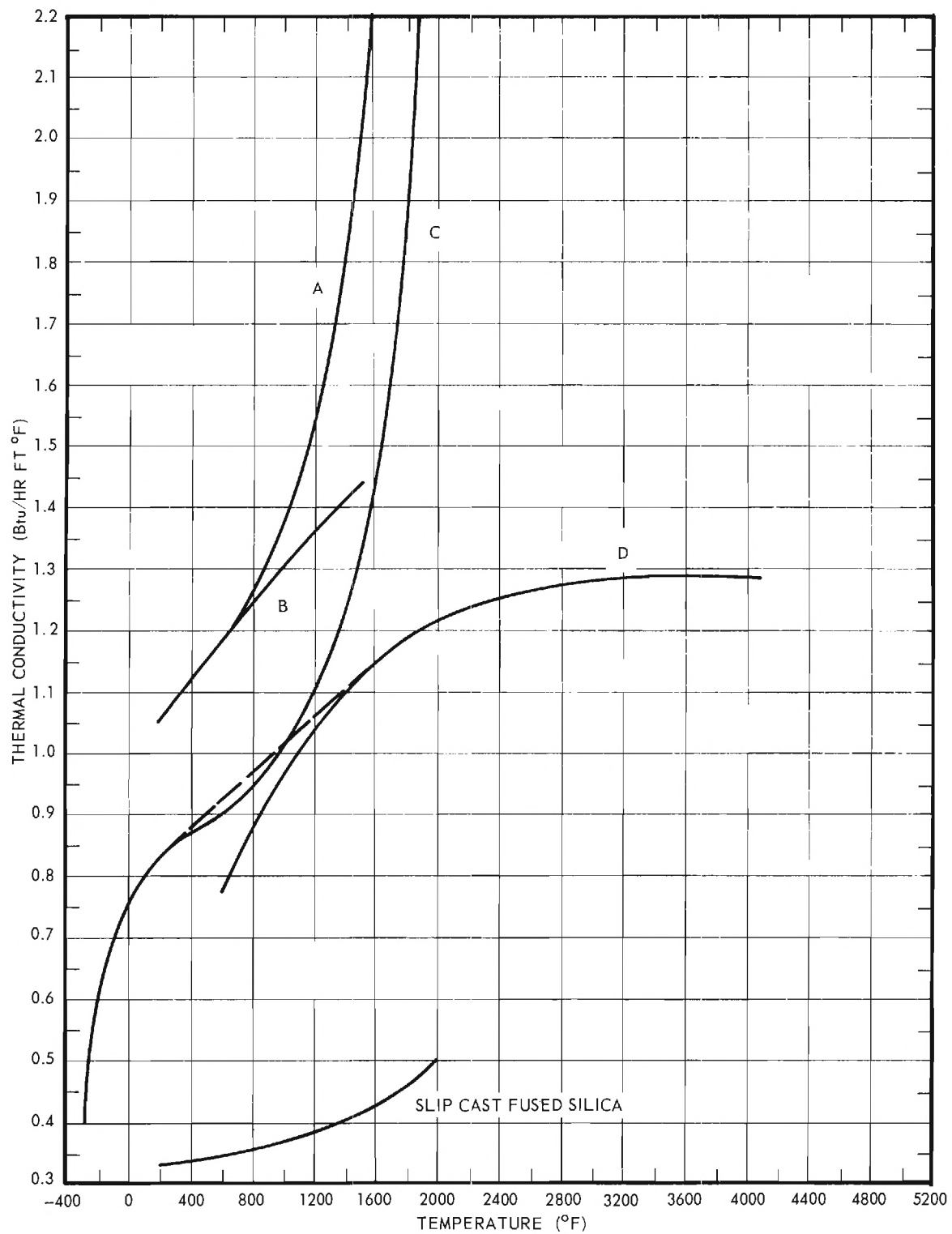


Figure 38. Thermal Conductivity of Fused Silica.

The thermal conductivity of slip-cast fused silica is also shown in Figure 38 (17). As would be expected, slip-cast fused silica does have a significantly lower conductivity than transparent fused silica. The difference in total heat transfer through equal thicknesses of the two materials is strikingly shown by comparison of Curve A, which includes direct radiation, for transparent fused silica and the curve for slip-cast fused silica which does not transmit radiant energy.

§ 5.2 Emissivity

The emissivity of a substance is dependent on a number of variables including surface condition, microstructure in the case of a transparent or translucent material, the exact conditions of the measurement, sample orientation, etc. These variables are often difficult to define and, in addition, experimental values may differ somewhat merely as a result of the method of measurement ^{1/}.

Early measurements of the emissivity of transparent fused silica were made by Pirani (14). These measurements were relative only and not of a high degree of accuracy. Figure 39 shows the results of later measurements of the total normal emissivity of transparent fused silica (1,7). The curve shown for translucent fused silica is from Pirani's original work (14) which has not been verified by more recent studies and is of uncertain accuracy.

Figure 39 also shows an estimate of the effective emissivity of slip-cast fused silica determined from comparative optical and radiation pyrometry (18). These values were drawn from limited preliminary data and must be considered only an approximation.

The data of several investigators have been combined to indicate the spectral variation of the emissivity of fused silica (8). Broad dips occur at approximately 3 and 9 microns and the emissivity becomes zero below about 2.5 microns.

§ 5.3 Heat Capacity

Accurate techniques for the measurement of heat capacity have been available for many years. As a result and since the heat capacity of fused

^{1/}These experimental values are more properly called emittance rather than emissivity. Use of the preferable term, emittance, is not yet widespread and the older terminology is used herein to avoid confusion.

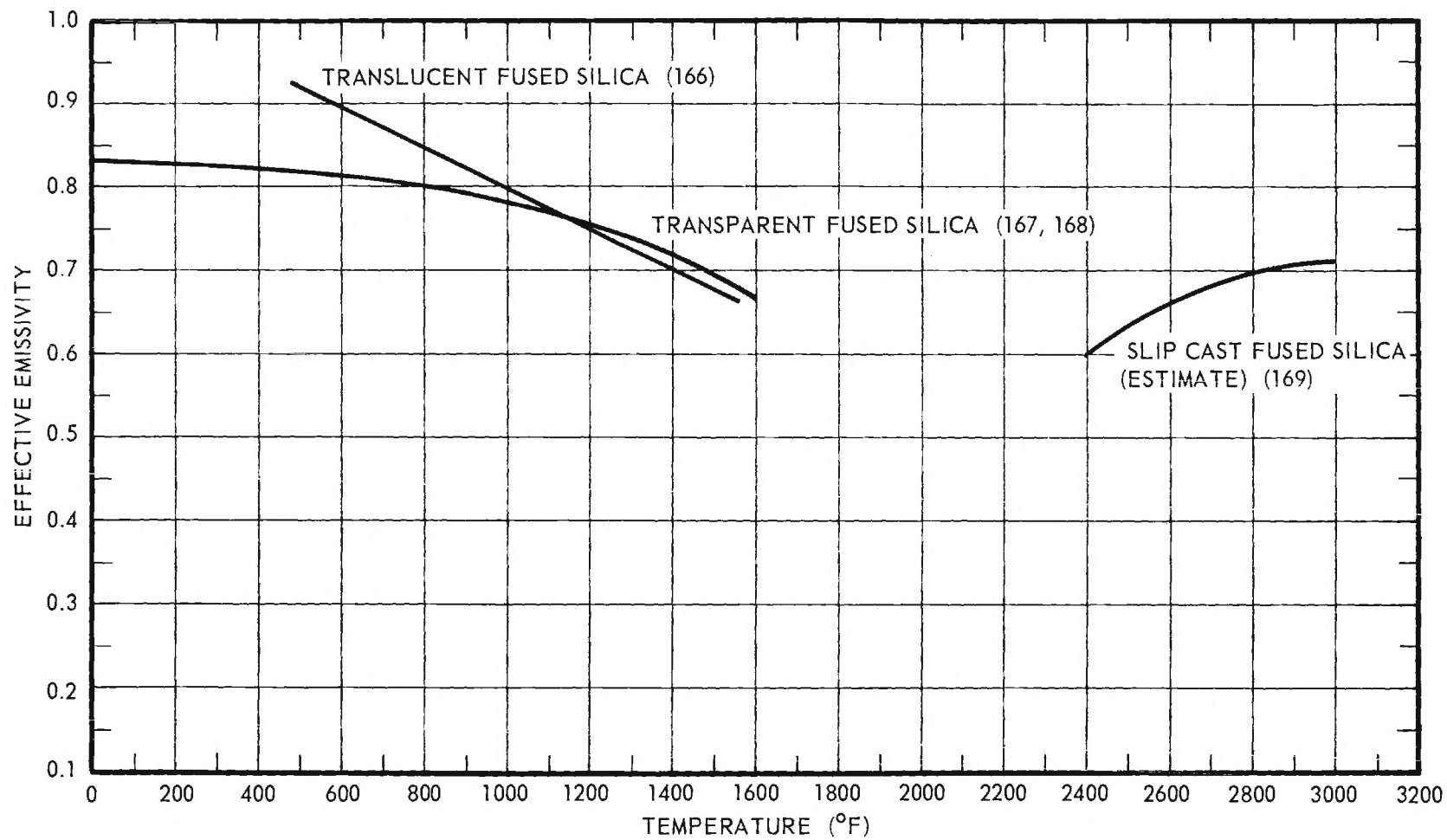


Figure 39. Emissivity of Fused Silica.

silica varies little with its form, values in the literature generally agree well (4,12,13). The heat capacity data shown in Figure 40 were drawn from the JANAF Thermochemical Data compilation (4).

§ 5.4 Enthalpy

Since heat capacity experiments are usually based on measurements of the change in enthalpy, enthalpy data will show the same agreement as heat capacity data. The data for the enthalpy plot of Figure 41 were taken from the JANAF tables (4).

§ 5.5 Heat and Free Energy of Formation

Since the heat of formation is usually determined indirectly, by measurement of various heats of reaction, values of both the heat and free energy of formation of fused silica in the literature vary by approximately 5 per cent (2,4,6,10,16). The values shown in Figure 42 were drawn from the JANAF tables (4).

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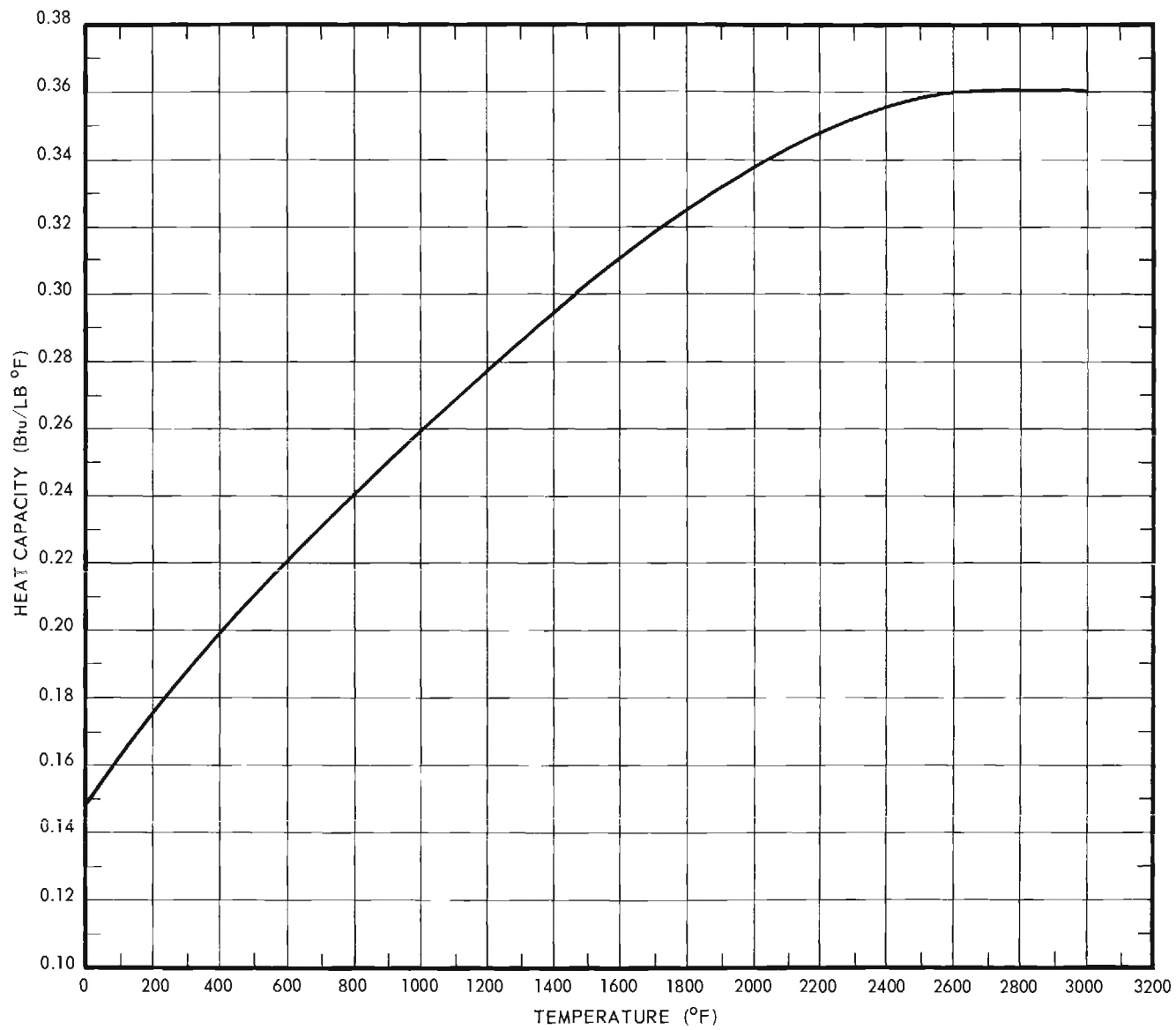


Figure 40. Heat Capacity of Fused Silica.

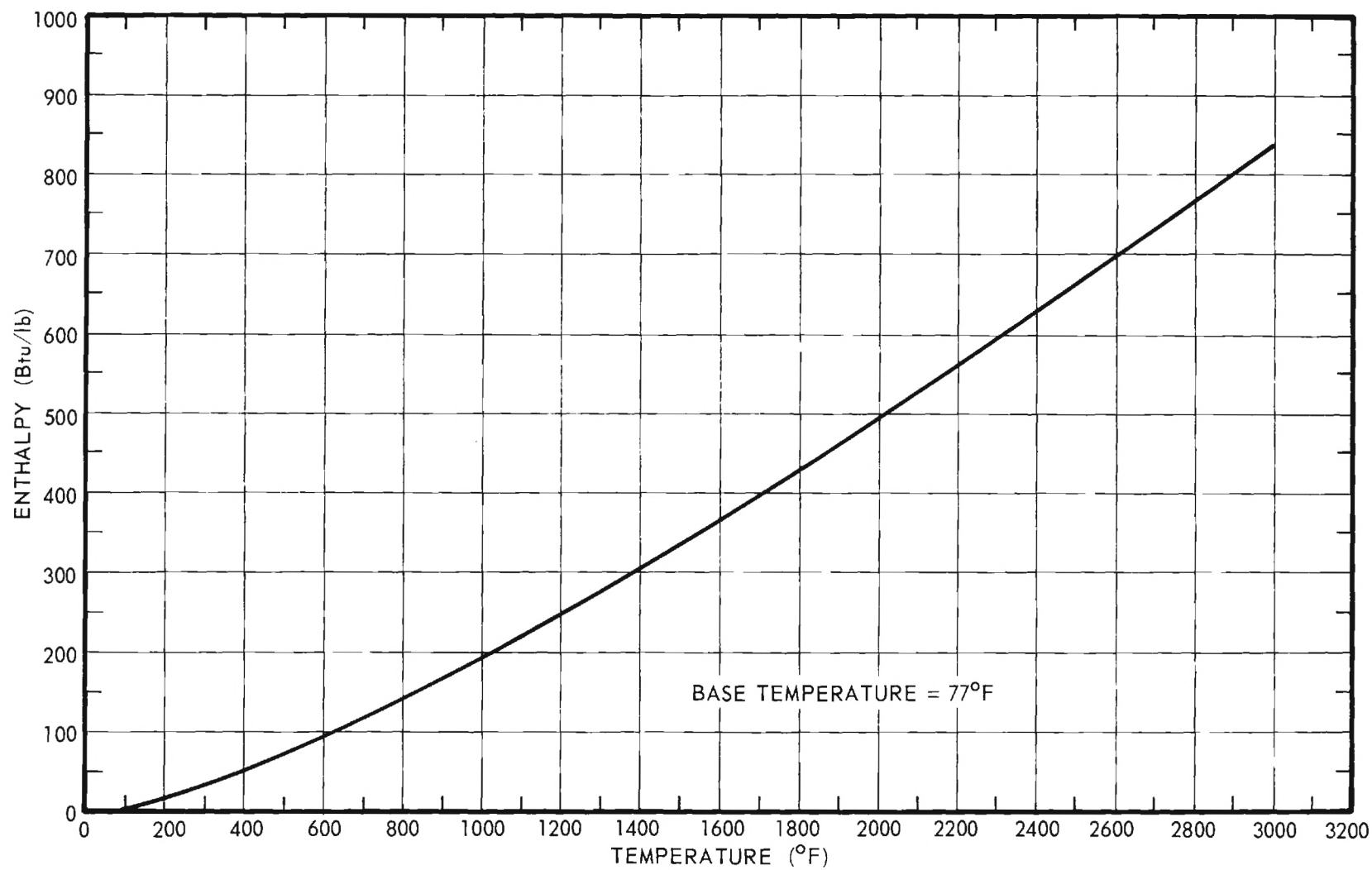


Figure 41. Enthalpy of Fused Silica.

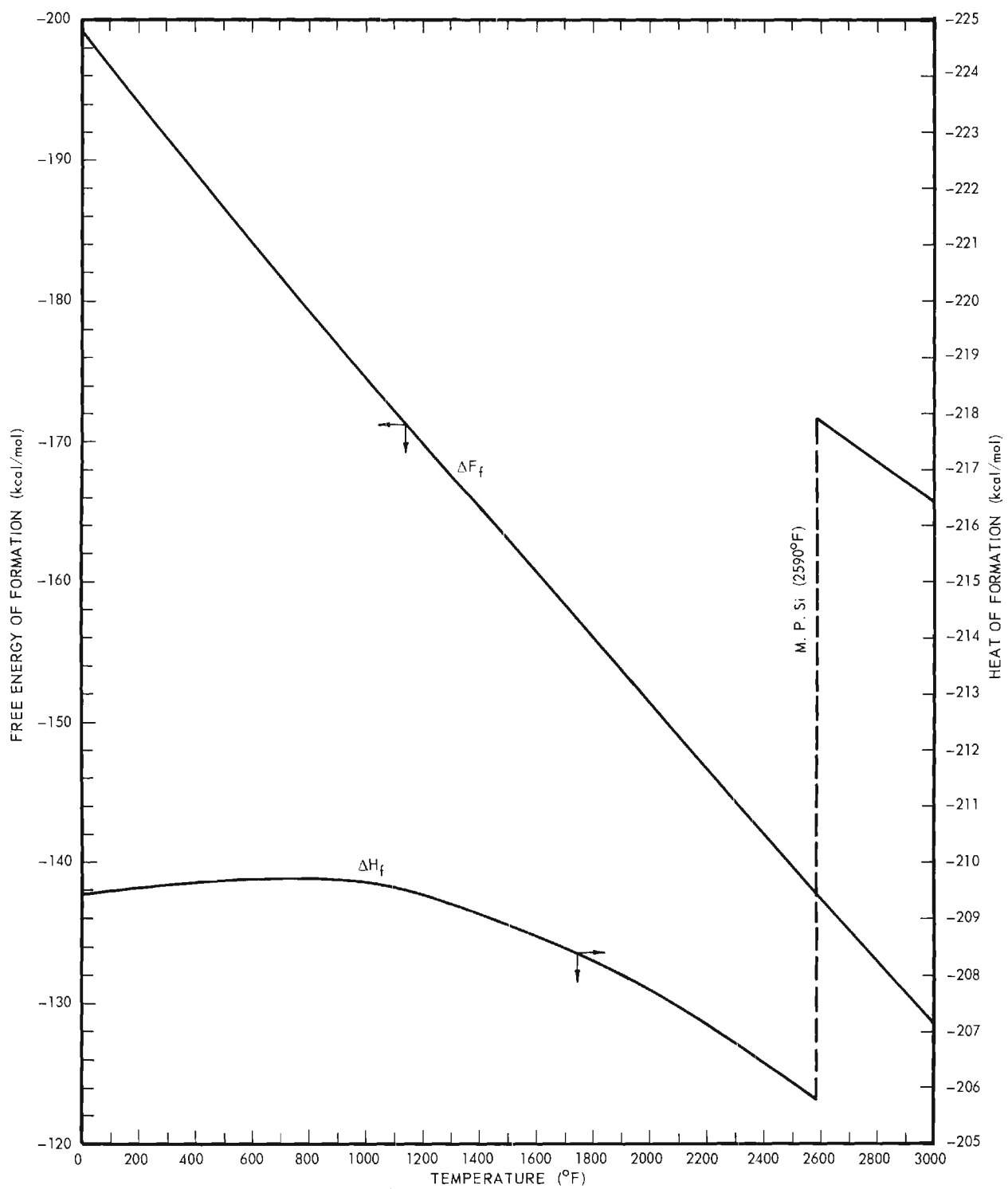


Figure 42. Heat and Free Energy of Formation of Fused Silica.

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CHAPTER VI

DEVITRIFICATION

- § 6.1 Introduction
- § 6.2 Devitrification Products
- § 6.3 Devitrification Mechanism
- § 6.4 Devitrification Rate
- § 6.5 Effects of Manufacturing Process
- § 6.6 Impurity Effects
- § 6.7 Influence of Atmosphere
- § 6.8 Structural Effects of Devitrification
- § 6.9 Effects of Devitrification on Physical Properties
- § 6.10 Specification of Maximum Service Temperature
- § 6.11 Shock Loading
- § 6.12 References for Chapter VI

§ 6.1 Introduction

Fused silica is thermodynamically unstable and tends to revert to one of the crystalline forms, usually cristobalite. The free energy difference favoring rearrangement of the silica tetrahedra into an extended, ordered crystal must be small according to Zachariasen's hypothesis of glass formation (25). While accurate measurement is difficult, the free energy change is probably less than 2 to 3 kcal per mole.

In order for cristobalite to form from fused silica, considerable motion of the silica tetrahedra is obviously necessary. The exceptionally high viscosity of fused silica indicates the high degree of association and lack of free mobility of the tetrahedra. This lack of mobility and the low driving force associated with the small free energy difference cause the kinetics of crystallization to be immeasurably slow at low temperatures. As the temperature increases, however, the viscosity decreases and the silica tetrahedra become more mobile. Reversion to a crystalline form is then more rapid and the fused silica can crystallize, or devitrify, in a reasonably short period of time.

The maximum temperature at which fused silica can be used is not ordinarily determined by softening and loss of strength but by the great increase which occurs in the devitrification rate. Proper application of fused silica thus demands an understanding of the factors which influence the devitrification rate and of the effects accompanying devitrification. An attempt is often made in materials handbooks to summarily discharge concern for devitrification by asserting that "fused silica may be used below 2200° F," or some similar temperature, "at which point it devitrifies." Such statements are responsible for gross overestimates in some cases and gross underestimates in others of the temperature limits governing application of fused silica. This misconception must be thoroughly overcome before any attempt is made to evaluate fused silica for a particular application.

Recent work by Ainslie, et al, (1) and Wagstaff (23) has served to clarify the devitrification process to a great extent. Only a sufficient survey of the devitrification phenomenon is presented here to give an idea of the scope of the problem. Recourse to Ainslie and Wagstaff is strongly recommended for anyone who works extensively with fused silica.

§ 6.2 Devitrification Products

Cristobalite is the usual product of the devitrification of fused silica and will form under any ordinary circumstances from devitrification of any commercial form.

Impurities can promote the formation of devitrification products other than cristobalite, but apparently only if their concentrations are in excess of about 0.5 per cent. Rieck indicated that monovalent impurity ions lead to tridymite while bivalent ions lead to cristobalite (17). Coquerelle found that mixtures of quartz and cristobalite form if the alkali impurity content is less than 0.5 mole per cent but that tridymite forms at higher impurity levels (8). Flörke showed that water vapor at high pressures results in the formation of tridymite instead of cristobalite (9). In studies by Bailey (2) and Schulman, et al (18), calcium caused quartz to be formed as a major devitrification product along with cristobalite.

A few investigators have found quartz as the principal devitrification product in fused silica of low impurity content (2, 19). Neither the effects

of firing atmosphere nor of residual crystalline material have been studied in detail and it is possible that quartz could result from unconventional heat treatment or from heating in a reducing atmosphere, as suggested by Balygin (3).

§ 6.3 Devitrification Mechanism

As discussed in more detail in the following sections, impurities within the fused silica and oxygen and water vapor in the atmosphere accelerate the rate of devitrification. Since both effects are more pronounced at the surface, cristobalite formation within the solid is rare and devitrification of glass-worked fused silica commonly proceeds from the surface inward (1).

Since slip-cast fused silica is porous, the atmosphere surrounds each particle and each devitrifies from its surface inward. This has the effect of producing devitrification throughout the specimen at much the same rate. The outer surface layer will still show a higher devitrification rate, however, since impurities will migrate from the plaster mold to the sample surface during casting ^{1/}. The thickness of this outer layer of rapid devitrification is small and the bulk of the sample crystallizes at a reasonably uniform rate.

§ 6.4 Devitrification Rate

Under ordinary conditions, the devitrification of glass-worked fused silica proceeds by an initial period of short duration, during which the surface is converted to cristobalite at a constant rate, followed by a diffusion controlled growth in which the depth of penetration of the cristobalite layer increases linearly with time (23). The devitrification rate of General Electric Type 204A fused silica, which has a low impurity and water content, is shown in Figure 43 (1).

Since each of the particles in the slip-cast fused silica undergoes simultaneous cristobalite growth, the devitrification rate is higher and somewhat more complex than that of transparent fused silica. Until the surface of each of the particles is completely covered with cristobalite, an analysis of the devitrification process shows that the volume fraction

^{1/}See § 3.6.

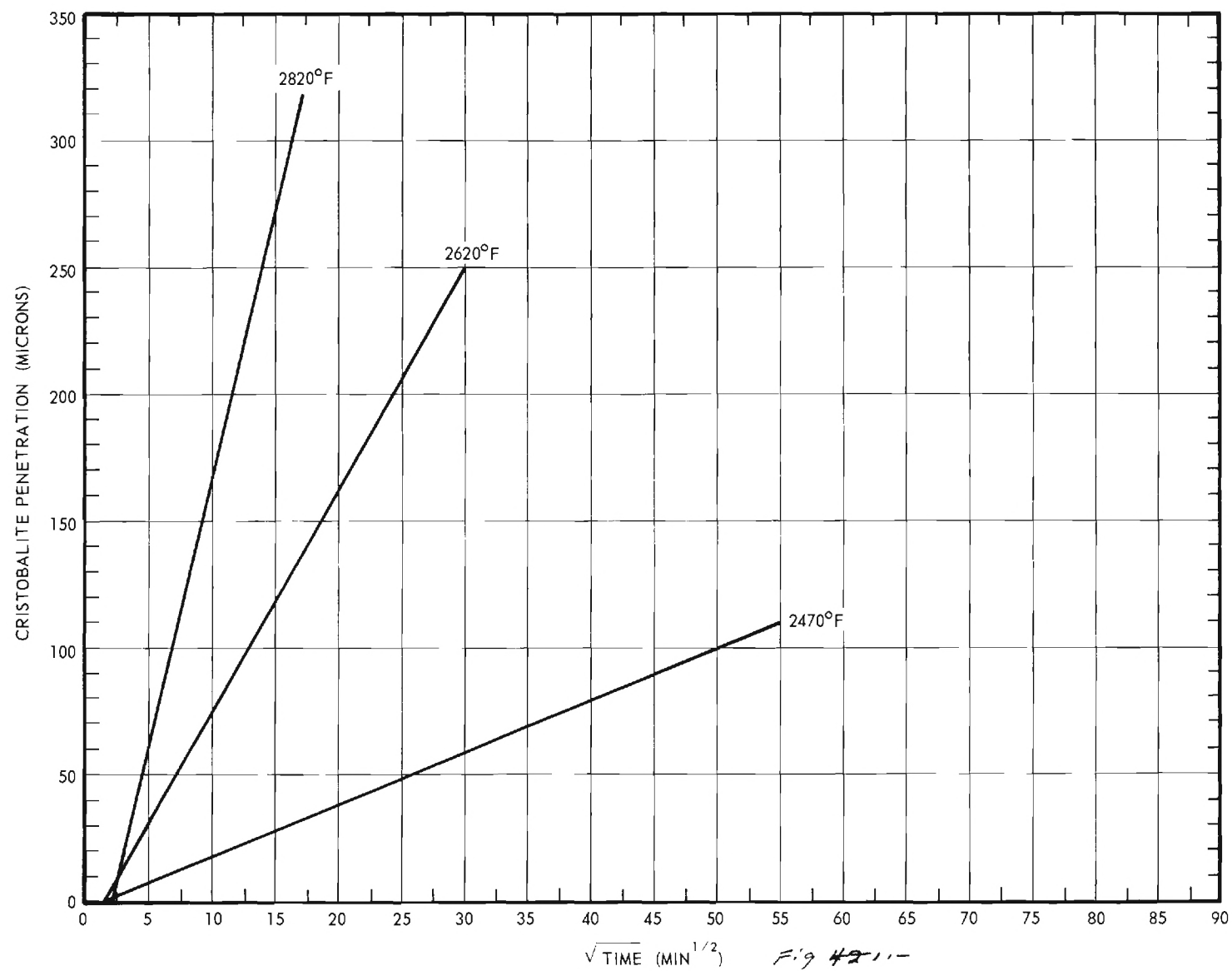


Figure 43. Devitrification Rate of General Electric Type 204 A Fused Silica.

converted to cristobalite varies with the cube of time (28). This analysis has been verified experimentally as shown in Figure 44. Following complete coverage of the particle surfaces with cristobalite, the bulk devitrification of slip-cast fused silica is best represented by a linear growth curve. This is illustrated in Figure 45 (26).

The cristobalite which initially forms from devitrification of fused silica is of a low degree of crystallographic order (20). Its x-ray diffraction pattern is thus less well defined than that of cristobalite grown at a higher temperature or heated for a longer period of time. As a result, silica which appears to be completely devitrified upon microscopic examination does not show a diffraction intensity characteristic of well ordered, pure cristobalite. On further heating, however, the diffraction trace is refined and the diffraction intensity approaches that of well ordered cristobalite. The curves of Figure 45 were determined by x-ray diffraction and are seen to level out below the point of complete cristobalite formation. This is undoubtedly caused by a combination of the x-ray effect discussed above and the decrease in the devitrification rate as the smaller particles become completely crystalline and no longer contribute to an increase in the amount of cristobalite present. As a result, the "true" cristobalite content at any time is probably slightly above the line in Figure 45. The extent of this difference cannot be quantitatively determined.

§ 6.5 Effects of Manufacturing Process

The technique used in the production of fused silica affects its devitrification rate in two ways. First, high temperature processes are likely to result in partial reduction of the silica as a result of the chemical equilibrium involved 1/ and the likelihood of a reducing atmosphere (4,23). This results in a non-stoichiometric product 2/ with an oxygen deficiency which has been shown less prone to devitrify (23). Since all structural fused silica is manufactured under somewhat similar conditions, at the present time, this effect is of minimal importance.

1/See § 4.12.

2/See § 2.12.

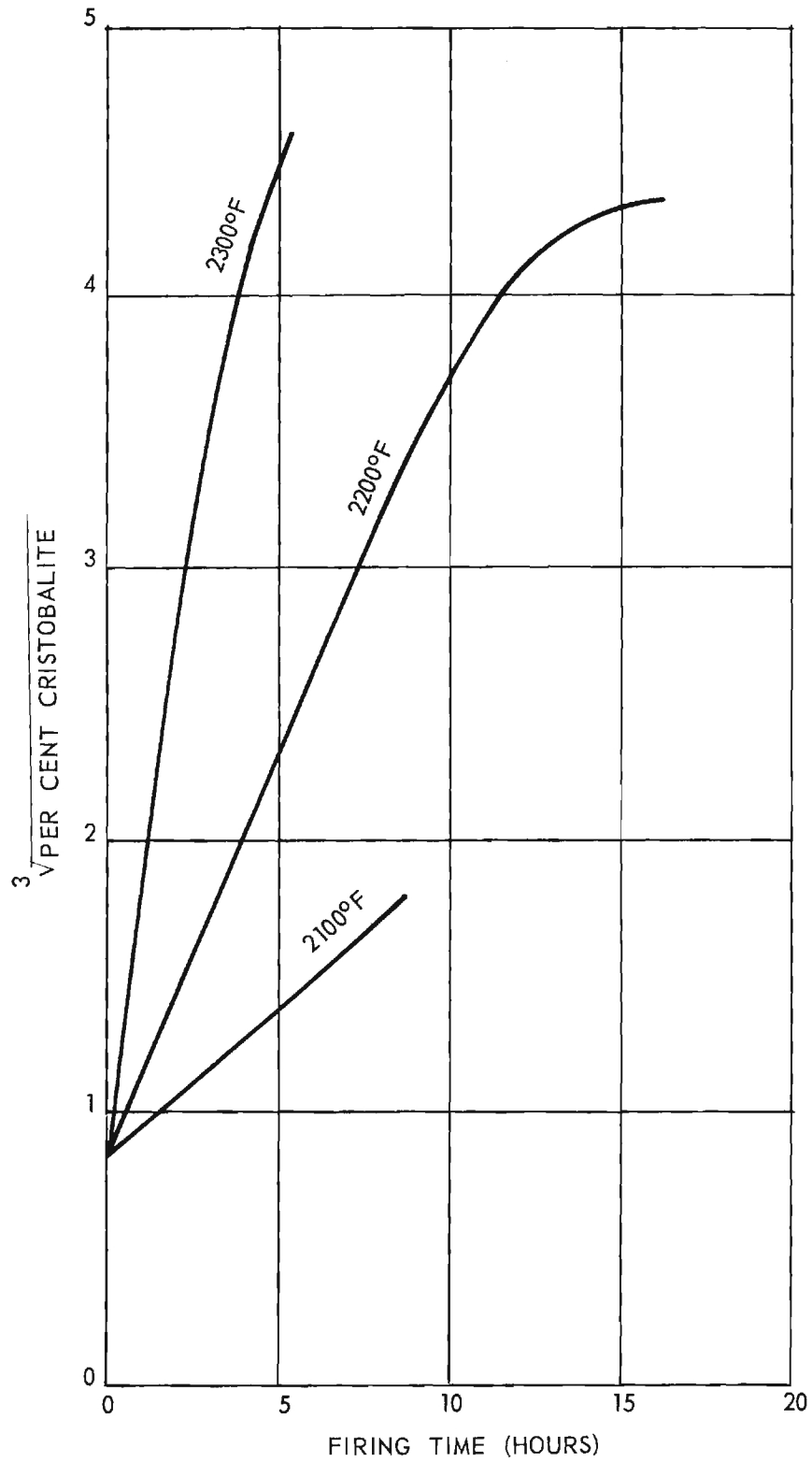


Figure 44. Bulk Growth of Cristobalite in Slip Cast Fused Silica Heated in Air.

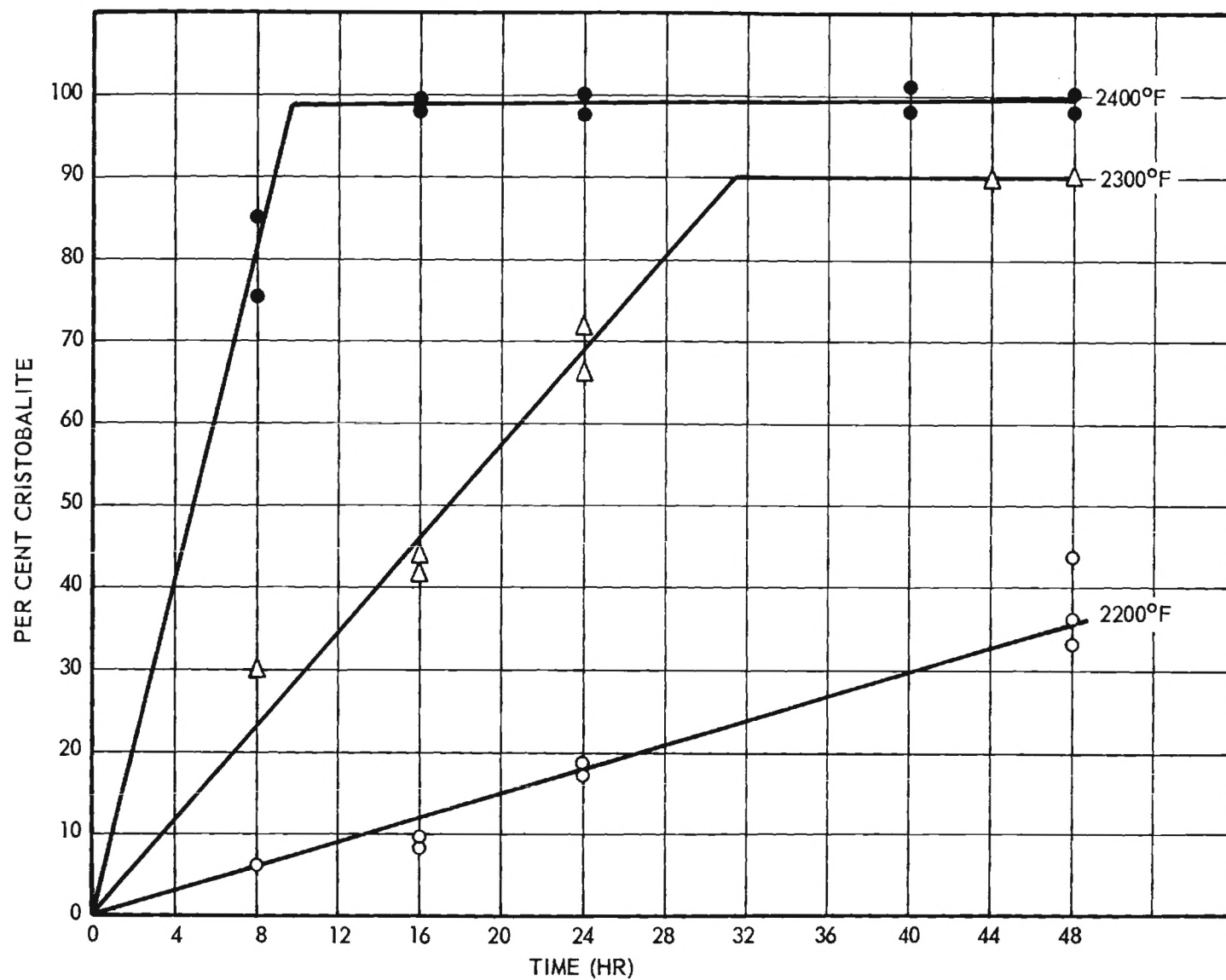


Figure 45. Bulk Growth of Cristobalite in Slip Cast Fused Silica Heated in Air.

The second influence is that of the water content or, more properly, the hydroxyl ion content of the fused silica ^{1/}. The water content is governed by the water vapor pressure during manufacture (10). The resulting hydroxyl ions cause scission of the silica chains and a concomitant lower viscosity or greater mobility of the silica tetrahedra (10) which, in turn, increases the devitrification rate (23).

Unless precautions are taken, the fused silica reaches roughly the same approach to water equilibrium during fusion and all electrically fused material will show about the same water content. In order to decrease the water content, water vapor must be excluded during melting or a post-melting vacuum anneal must be used to dry the rough melt. Since both of these approaches produce substantial increases in cost, and since normal electrical fusion produces a low water content, neither is used at the present time in the production of structural grades of fused silica and all commercial structural grades will have about the same water content.

While the commercial structural grades of fused silica do not differ appreciably in stoichiometry or water content, this is not true for the optical grades. Certain optical grades are oxidized and are of controlled water content. As a result, these materials may differ enough to show significant variations in devitrification rates.

§ 6.6 Impurity Effects

Impurities tend to increase the rate of devitrification of fused silica through decreasing the viscosity and increasing the mobility of the silica tetrahedra or through producing centers of ionic asymmetry which are effective in causing nucleation (24). Although occasional suggestions are found in the literature that Al_2O_3 (12) or B_2O_3 (11) suppress devitrification, this has been refuted (5,14). B_2O_3 serves rather to offset the effects of alkali impurities (5). A surface layer of alumina protects the fused silica from atmospheric gases which would otherwise increase the rate of devitrification (17) but doping silica with Al_2O_3 increases the devitrification rate (5).

^{1/}See § 2.13.

In general, the sequence of decreasing effect in promoting devitrification is (17):

K
Na
Li
Ba
Pb
Ca
Fe⁺²
Zn
Mg
Fe⁺³
Al
Ti

Since structural grades of fused silica are produced from sand of varying purity, products of different manufacturers may vary enough in impurity content to show different rates of devitrification. These differences cannot be generalized and the products should be evaluated individually on the basis of their analyses, particularly with respect to the alkali content.

Introduction of impurities by poor handling techniques is far more likely to be important in determining the devitrification tendency than is the impurity content of the fused silica itself 1/. Handling the material without gloves is almost certain to result in contamination of the surface with sodium. Heating a piece of transparent fused silica which has not been cleaned will often result in outlining fingerprints on the surface by localized devitrification. Care in maintaining cleanliness, the use of gloves in handling the silica, and avoiding any needless contamination is essential in working with fused silica.

§ 6.7 Influence of Atmosphere

Exposure of fused silica to oxygen or water vapor during heating results in more rapid devitrification than if the atmosphere is inert (1,23,27). Oxygen appears to act by conversion of the silica to a more nearly stoichiometric

1/See § 3.8, 3.12.

state, thereby enhancing extension of the cristobalite structure, while water both increases the approach to stoichiometry and decreases the viscosity (23).

Coating fused silica with a film of alumina serves to decrease devitrification since the alumina acts as a barrier to the diffusion of oxygen and water vapor into the silica (17). In the temperature range of application of fused silica, the alumina has little tendency to diffuse into the silica and devitrification is not promoted thereby. Much the same effect has been noted upon deposition of pyrolytic graphite and other "getters" on fused silica (1).

Although application of this principle to the protection of slip-cast fused silica may offer promise, no systematic attempt to take advantage of it has been reported. Incorporation of a film former or a material which would generate a reducing atmosphere might produce interesting results.

§ 6.8 Structural Effects of Devitrification

Since the densities of cristobalite and fused silica are nearly the same at high temperatures ^{1/}, devitrification does not result in noticeable structural changes until the silica is cooled (1). At least by the time the cristobalite inversion temperature is passed, high stresses develop in the devitrified layer and cracks appear. When the devitrified layer becomes approximately 1/16-inch thick in glass-worked fused silica, spallation occurs and the devitrified layer separates from the unchanged core (23).

In slip-cast fused silica, the structural effects of devitrification are less obvious. Perhaps since the porosity serves to terminate cracks, slip-cast fused silica seldom spalls upon devitrification. Bars may be completely devitrified with little apparent structural change although, of course, the properties are degraded as discussed in the following sections.

§ 6.9 Effects of Devitrification on Physical Properties

As mentioned above, cristobalite and fused silica have similar densities and similar thermal expansion coefficients in the devitrification temperature

^{1/}See § 2.5.

range. As a result, pronounced structural changes do not occur until the material is cooled. Any discussion of the effects of devitrification must then clearly distinguish between changes which occur after the silica is cooled and those which occur at temperature.

The fissures which develop during cooling of devitrified fused silica result in the expected changes in properties. The strength (13), the rigidity (6), and the thermal conductivity (16) all decrease in devitrified glass-worked fused silica. Much the same effects are noted in slip-cast fused silica 1/ although available data do not permit quantitative comparison with the changes in glass-worked fused silica.

On reheating, devitrified fused silica shows a strong tendency toward recovery of its strength 2/ (6) and presumably of thermal conductivity as well, although the recovery will not be complete until the flaws are healed by sintering. This occurs as a result of expansion of the cristobalite on heating, re-filling the fissures generated during cooling (6).

Although no studies have been made to verify the assumption, there is no reason to expect the strength of devitrified fused silica to decrease until the specimen is cooled. The recovery of strength noted when devitrified fused silica is reheated is strong evidence in support of this conclusion. The observation of increased thermal conductivity in devitrified fused silica before cooling (15) is a further indication that coherency is maintained between the cristobalite formed and the residual fused silica.

The viscosity of fused silica increases as devitrification occurs. Approximately an order of magnitude increase accompanies the formation of about 15 per cent cristobalite (6, 7). The creep strength shows a corresponding increase.

In keeping with the observations noted above, until further studies are carried out the effects of devitrification must be assumed to be:

Before Cooling:

1. No change or a possible increase in strength.

1/See § 3.15.

2/See § 4.3.

2. Approximately the same thermal shock resistance in the high temperature range.
3. Increased creep strength.
4. Increased thermal conductivity.
5. Changes in other properties which will tend toward the properties of cristobalite.

After Cooling:

1. Decreased strength.
2. Decreased thermal conductivity.
3. Increased porosity.
4. General degradation of other properties.

On Reheating:

Partial recovery of all properties with the extent of recovery increasing with increasing temperature and time.

The temperature at which degradation of properties is first observed is not well defined, and the properties will probably decrease gradually over a broad temperature range. A more or less sudden change can be expected at approximately 500° F, the cristobalite inversion temperature, but some change can be expected at higher temperatures. A noticeable strength decrease on cooling has been demonstrated at temperatures as high as 1300° F (13).

§ 6.10 Specification of Maximum Service Temperature

Frequent statements are found in the literature that fused silica can be used at temperatures up to a fixed level, usually around 2100 to 2200° F. Statements such as this are gross oversimplifications and may be quite misleading. In fact, fused silica may be used with success at temperatures as high as about 3000° F in some applications while others may require the temperature to be kept below 1900° F.

The maximum temperature at which fused silica can be used satisfactorily is not fixed but depends on the planned duty cycle. In general, this temperature is set either by devitrification or by a decrease in strength

with temperature. The controlling factor is, of course, not set by choice but by exclusion.

The principal points which must be remembered in setting a maximum temperature for a given application are that devitrification is a rate controlled process and that the mechanical properties should show little degradation upon devitrification until the silica is cooled. As a consequence of these two points, the permissible operating temperature is increased by:

1. Short operating time.
2. Single cycle use, i.e. the silica is not subjected to cyclic operation involving a lower temperature below perhaps 1300° F.
3. Operation in vacuum or in an inert atmosphere.
4. (Possibly) Exposure to nuclear radiation 1/.

If these factors are such as to render devitrification unimportant in a particular application, then the maximum operating temperature is set by softening and the loss of mechanical properties. In this case, the permissible operating temperature will be relatively high, probably in the range of 2700° F. If these factors are such as to make devitrification important, the maximum operating temperature must be kept low enough to prevent the critical extent of devitrification from occurring. This temperature will be lower than that in the first case and must be decreased as the service lifetime increases. This will probably bring the allowable temperature below 2200° F for glass-worked silica and below 2100° F for slip-cast fused silica.

Unfortunately, no set rules can be stated which will permit formal calculation of the maximum operating temperature. At the present time, this remains a matter of engineering judgement. The application of the factors involved is illustrated in the following examples:

a. Radome for Interceptor Missile. This application involves a short operating time, a duty cycle of only one heating, and probably

1/See § 7.17.

development of a steep thermal gradient through the silica. The most important factor in this application is that the fused silica is continuously heated during its entire duty cycle. As a result, while the operating life time may be sufficiently short to avoid devitrification, it will be unimportant even if it does occur since the fused silica is not cooled enough to cause an appreciable loss of strength. Furthermore, the steep thermal gradient places the majority of the silica in the range of high strength although the surface may "melt" or even sublime. Even if it softens the surface will show a low tendency to deform as a result of the very high viscosity of molten fused silica. The allowable operating temperature of the surface of the radome may then be set far in excess of the 2200° F limit which is widely listed for fused silica. A limit, in this case, of 3000° to 4000° F at the surface is not unreasonable.

b. Loading Hearth in Gas Heated Furnace. This application involves the worst conditions for fused silica. The operating time is long, cyclic heating and cooling are planned, and the environmental combustion gases are likely to be high in water vapor. In order to avoid loss of strength in the hearth, the fused silica must be kept well below the usual "limit" of 2200° F. Complete safety may restrict operation to a temperature range as low as 1800° to 1900° F.

Two exceptions should be noted even in this case. First, if slip-cast fused silica is used, extensive devitrification will not cause spalling although cracks will develop. As a result, if the hearth does not require high strength, application of fused silica at a higher temperature may be considered. Second, if the hearth is not difficult to replace, use of slip-cast fused silica may still be more economical than other refractories although replacement proves necessary after a few cycles. If reasonably frequent replacement is feasible, then, the permissible temperature may be increased.

These two examples represent extremes in the application of fused silica. The considerations applied, however, pertain with equal force to any other application. Reasoning such as that outlined should be applied in evaluating any elevated temperature use of fused silica.

§ 6.11 Shock Loading

In addition to the more conventional factors discussed above, mention should be made of the possibility of devitrification under shock-wave compression. This possibility has not yet been well explored but it may be of importance in a few unusual applications.

Viard reported an indication of crystallization in fused silica as a result of a 135 kilobar shock wave (21). If this proves to be a valid observation, the mechanism will undoubtedly be found complex since Wackerle found that crystalline quartz was transformed to the fused state under high shock pressures (22).

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NOTE: The following references are to reports issued under this contract.
See Appendix B for complete listing.

26. Progress Report No. 1 p. 46.
27. Summary Report No. 1 p. 34.
28. Quarterly Report No. 4 p.4, Quarterly Report No. 5 p. 7.

CHAPTER VII

IRRADIATION BEHAVIOR

- § 7.1 Introduction
- § 7.2 Effects of Irradiation on Different Forms of Silica
- § 7.3 Atomic Structure of Irradiated Fused Silica
- § 7.4 Macrostructural Changes
- § 7.5 Cross Section
- § 7.6 Effects on Strength
- § 7.7 Hardness
- § 7.8 Shear Modulus
- § 7.9 Young's Modulus
- § 7.10 Density
- § 7.11 Thermal Expansion
- § 7.12 Thermal Conductivity
- § 7.13 Effects of Annealing
- § 7.14 Dielectric Constant and Loss
- § 7.15 Effects of Irradiation on Devitrified Fused Silica
- § 7.16 Optical Effects
- § 7.17 Irradiation at Elevated Temperatures
- § 7.18 References for Chapter VII

§ 7.1 Introduction

Fused silica has been used for years in encapsulation of specimens to be irradiated in nuclear reactors. This use was prompted by its lack of structural changes under irradiation, chemical inertness, low cross section, and low permeability to gases. In spite of the widespread experience with fused silica in encapsulation, little consideration has been given in the United States to its use as a structural material in radiation fields. Most of the studies of fused silica under irradiation involve potential optical applications or use as a convenient material in fundamental studies of radiation damage.

This chapter is devoted principally to the few studies bearing on potential structural applications of fused silica in nuclear reactors and

other radiation environments. Only brief reference is made to the vast literature concerning the optical changes in irradiated fused silica.

An excellent review of the literature on irradiation effects in fused silica was published by Primak (20). This article is strongly recommended for its critical comparison of experimental results and discussion of the theories of radiation damage in silica as of 1960. Ancillary information in the earlier literature on irradiation of quartz may be located through a bibliography compiled by Bechmann (2).

§ 7.2 Effects of Irradiation on Different Forms of Silica

Irradiation of quartz to a dose of 10^{19} nvt $\frac{1}{\text{cm}^2}$ results in changes of its x-ray diffraction pattern consisting of slightly increased diffraction peak intensity (14). Further irradiation to 7×10^{19} nvt produces radical changes showing an entirely different crystallographic symmetry and the appearance of halos characteristic of amorphous materials. A substantial degree of crystallinity remains at a dose of 1×10^{20} nvt (28), but by a dose of 2×10^{20} nvt quartz is transformed to a structure similar to thermally fused silica and identical to fused silica irradiated to the same level (18).

Cristobalite shows a decrease in the α - β inversion temperature and a decrease in density upon irradiation to 1.3×10^{19} nvt (15).

Quartz, cristobalite, tridymite, and fused silica are all transformed into an identical material by irradiation to approximately 2×10^{20} nvt (30). This material is quite similar to thermally fused silica (22) but not identical as discussed in the following section.

§ 7.3 Atomic Structure of Irradiated Fused Silica

Irradiated fused silica, as well as irradiated crystalline silica, is physically similar to but structurally distinct from unirradiated fused silica. These distinctions are most clearly shown by measurements reflecting atomic arrangement and do not become manifest from determination of the physical properties, as discussed in the following sections.

The x-ray diffraction pattern of fused silica is slightly altered by irradiation (17). The main peak is broadened and slightly shifted.

The refractive index of irradiated fused silica increases from approximately 1.457 to approximately 1.467 (23).

$\frac{1}{\text{nvt}} = \text{Neutrons/cm}^2$.

The infrared reflection spectrum of fused silica is altered upon irradiation (23). The position of the maximum is shifted slightly and measurable changes occur in the lower frequency spectrum.

Simon developed curves of the radial electron density distribution for irradiated quartz, which gave the same x-ray scattering curve as irradiated fused silica, and for unirradiated fused silica (22, 23). He found that the Si-O distance is not altered by irradiation but that the Si-Si distance decreases from 3.03 to 2.99 Å. This indicates a decrease in the Si-O-Si bond angle to about 138°.

Gossick concluded, from a study of optical extinction bands, that free silicon particles are produced by irradiation of quartz (13). These results were confirmed to some extent by Weissmenn and Nakajima who demonstrated the generation of interstitial silicon by rupture of Si-O bonds under irradiation (29). These authors showed that irradiation of quartz produces defect clusters which increase in number upon further irradiation until they interact, forming a hexagonal-like defect structure which is very resistant to annealing at 830° F.

Although doubts have been expressed (31), perhaps the prevailing view is that thermal spikes are principally responsible for the changes noted in irradiated silica (20, 23, 29). These thermal spikes, producing temperatures of about 18,000° F for 10^{-11} seconds (23) can account for the slight increase in order observed in fused silica as well as the significant decrease in order in the crystalline forms, producing the same final material under irradiation (20).

The studies discussed above indicate that irradiated fused silica is structurally similar to unirradiated fused silica but with slightly refined short range order and at least the possibility of some free silicon. No gross changes appear in the molecular arrangement, however.

§ 7.4 Macrostructural Changes

Thin plates of fused silica have been reported to warp under irradiation (7, 22). Primak and Edwards found that most irradiated specimens are internally stressed (21). They suggested that this results from radiation gradients established by scattering and absorption. More often, however, transparent

fused silica acquires a slight blue or violet coloration (11) and shows no obvious structural changes at all (17).

Slip-cast fused silica irradiated to approximately 4×10^{20} nvt shows no warping or any obvious structural change (10). No coloration is noted but the presence of the internal reflecting surfaces associated with the porosity would mask any such effects.

§ 7.5 Cross Sections

The total cross section of fused silica has been measured for 300° K neutrons (C neutrons) (3). The measured cross section is 8.0 ± 1.0 barns compared with 10.2 barns calculated from atomic contributions. This difference shows that molecular interference does occur as would be expected from the light atoms involved. This interference should decrease with increasing neutron velocity.

The additive cross sections for 2200 meter per second neutrons are tabulated in Table IX.

TABLE IX
2200 M/S CROSS SECTIONS OF FUSED SILICA

Absorption (Additive)	0.161 Barns
Macroscopic Absorption (Additive)	0.0035 cm^{-1}
Scattering (Additive)	10.1 Barns
Total (Additive)	10.2 Barns
Total (Measured, Ref. 3)	8.0 Barns

§ 7.6 Effects on Strength

Thompson found that irradiation at 212° F to 2.4×10^{18} nvt and at -321° F to 1.6×10^{18} nvt left the strength of transparent fused silica unchanged within ± 10 per cent (26).

Fleming irradiated slip-cast fused silica to calculated dose levels of from approximately 2×10^{20} to 6×10^{20} nvt (10). The irradiated specimens were transverse tested and compared with unirradiated specimens. The strengths of the two sets of specimens did not differ at greater than the 75 per cent

level of confidence, so that the irradiation cannot be said to have produced any significant change.

§ 7.7 Hardness

Gorski irradiated fused silica with x-rays to a dose level of 3×10^7 (12). An increase in microhardness of 3.4 per cent was measured.

§ 7.8 Shear Modulus

Strakna, et al, irradiated fused silica to a dose of more than 5×10^{19} nvt (25). The room temperature shear modulus was increased by less than 1 per cent. The shear modulus was more stable with temperature over the range -360 to 80° F than that of unirradiated fused silica and showed a lower dependence on pressure.

§ 7.9 Young's Modulus

Bopp, et al, irradiated fused silica to doses ranging from 8×10^{19} to 4×10^{20} nvt (4). The Young's modulus was unchanged within 5 per cent in any irradiation.

§ 7.10 Density

Primak and Edwards isolated three effects capable of causing density changes in the irradiation of fused silica (21). The first is destruction of any residual crystallinity 1/ by fast neutrons. This is complete by about 3×10^{20} nvt and produces a density decrease. The second is compaction of the fused silica structure by fast neutrons which reaches a maximum of about 3 per cent at a dose of about 3×10^{19} nvt. The third effect is an initial compaction by ionizing radiation which quickly reverses after a brief irradiation. Following the initial compaction, ionizing radiation causes an expansion. After saturation of all effects, a net increase in density of approximately 2.3 per cent is observed.

Azizov and Starodubtsev measured the density changes in γ -irradiated fused silica (1). A density decrease of approximately 2 per cent was noted at a dose of 9×10^7 r. Upon further irradiation to 1.8×10^8 r, the density

1/See § 2.9.

returned to the original value and no further change was observed to 3.6×10^8 r.

§ 7.11 Thermal Expansion

Simon measured the thermal expansion coefficient of fused silica between room temperature and 400°F after irradiation to 1.4×10^{20} nvt (24). The value determined was $3 \times 10^{-7} \text{ } ^\circ \text{F}^{-1}$ which falls well within the limits for unirradiated fused silica 1/.

§ 7.12 Thermal Conductivity

Cohen studied the effect of irradiation on the thermal conductivity of fused silica in the temperature range from -456 to -442°F (5). The thermal conductivity increased linearly with dose, becoming doubled at the highest dose used, 6×10^{19} nvt (19).

Bopp, et al, measured the room temperature thermal conductivity of fused silica irradiated to doses of 3×10^{19} to 1.6×10^{20} nvt (4). The thermal conductivity was unchanged within 5 per cent in all irradiations.

§ 7.13 Effects of Annealing

In general, irradiated fused silica tends to recover its original properties on annealing. A suggestion was originally made by Wittels and Sherrill that the disordered silica formed by heavy irradiation of quartz, cristobalite, tridymite, or fused silica is transformed by annealing to quartz (30). Primak pointed out that this observation resulted from residual crystalline nuclei in the material studied (20) and Mayer and Lacomte showed that irradiated quartz may be transformed to fused silica or reconverted to quartz on annealing, depending on the irradiation dose and temperature (18).

§ 7.14 Dielectric Constant and Loss

Thomasch and Pentz studied the effects of irradiation on the dielectric constant of fused silica (27). The dose received was not estimated but the silica was intensely colored and the dose was presumably quite heavy. The loss and dielectric constant were measured over a frequency range from 2 to

1/See § 4.8.

300 kc. and a temperature range from 330 to 580° F. The values obtained were identical to those obtained with unirradiated fused silica.

§ 7.15 Effects of Irradiation on Devitrified Fused Silica

Fleming evaluated the effects of irradiation on partially devitrified slip-cast fused silica (10). Specimens were fired for 48 hours in air at 2500° F to produce extensive devitrification. After irradiation, x-ray diffraction failed to show any cristobalite remaining in samples exposed to an estimated dose above 3×10^{20} nvt. Samples which initially contained from 21 to 88 per cent cristobalite retained from 3 to 8 per cent cristobalite after a dose of 2×10^{20} to 3×10^{20} nvt. Destruction of the cristobalite produced no changes in the strength of the specimens.

§ 7.16 Optical Effects

Many studies have been made of the effects of radiation on the optical properties of fused silica. An annotated bibliography is available which covers the work from 1949 to 1961 (9). Crawford reviewed the literature prior to 1958 in two papers (7, 8) and Lell summarized a part of the more recent literature (16).

Probably the only optical property of concern to those interested in structural uses of fused silica is the transmission in the visible light range. Colp and Woodall found no effect on the transmission after 10^{10} r. of γ radiation and 10^{16} nvt (6). They predicted that the visual properties would not be seriously altered up to 1.4×10^{17} nvt.

§ 7.17 Irradiation at Elevated Temperatures

Unfortunately, no studies have been made to determine the effects of irradiation of fused silica at elevated temperatures. Conjecture as to such effects is very speculative since the homogenizing effects of radiation 1/ and the crystallizing effects of temperature 2/ may not operate independently of each other. Unless some unusual interaction occurs, the combined effects might be expected to be suppression of devitrification by neutron irradiation

1/See § 7.10.

2/See Chapter 6.

and prevention of stress generation by the higher mobility at elevated temperatures. If this should prove to be the case, fused silica would certainly be an unusual material for applications in nuclear engineering. Elevated temperatures and irradiation in combination could offset the adverse effects which either has alone and fused silica might well have a broader range of application in reactor structures than in any other environment. There at least seems to be a possibility that fused silica would benefit from irradiation in strong contrast to the undesirable changes which occur upon irradiation of most other materials.

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CHAPTER VIII

CHEMICAL RESISTANCE

- § 8.1 Introduction
- § 8.2 Solid and Liquid Elements
- § 8.3 Gases
- § 8.4 Oxides
- § 8.5 Fluorides
- § 8.6 Chlorides
- § 8.7 Iodides
- § 8.8 Sulfides
- § 8.9 Cyanides
- § 8.10 Borates
- § 8.11 Carbonates
- § 8.12 Chromates
- § 8.13 Nitrates
- § 8.14 Phosphates
- § 8.15 Sulfates
- § 8.16 Hydroxides
- § 8.17 Acids
- § 8.18 Water
- § 8.19 Miscellaneous
- § 8.20 Prediction of Reactions
- § 8.21 References for Chapter VIII

§ 8.1 Introduction

The chemical resistance of fused silica probably covers a broader spectrum than any other engineering material. As far as general classes of chemicals are concerned, fused silica is attacked only by alkalis, alkaline salts, and hydrofluoric acid at moderate temperatures. At higher temperatures, phosphoric acid, metal oxides, and a few metals also react with fused silica.

While generalizations are useful in predicting chemical attack of fused silica, particular applications require more detailed evaluation. The following sections summarize data which are currently available to aid such

an evaluation. Since the methods employed in evaluating chemical corrosion vary so widely, summarizing quantitative information is more likely to be misleading than helpful. As a result, this summary is in qualitative terms only. Quantitative information concerning specific applications may be located through the literature cited or by inquiry to the commercial firms listed in Chapter XI. These firms have extensive experience in this area and can probably be much more helpful than any other single source of information.

In evaluating the resistance of fused silica to the materials listed below, caution must be exercised in defining the system. As an example, fused silica is resistant to attack by zinc but reacts with zinc oxide. In melting zinc in fused silica exposed to air, then, a reaction will be observed not with the zinc but with the oxide film formed on its surface. Similar problems arise if several chemicals are present in a mixture. The effects are not the sum of those of the individual chemicals but may be entirely different. The silica may be more resistant or more prone to attack by the mixture than by any individual component.

Unless noted, the actions listed are for the pure materials. Except for alkalis and phosphoric and hydrofluoric acids, aqueous solutions seldom show any tendency toward reaction with fused silica.

Following the specific evaluations listed in the following sections is a brief summary ^{1/} of the familiar methods which may be used to predict reactivity when experimental data are lacking.

In compiling this list, free reference was made to the trade literature, especially the excellent summary "About Vitreosil" prepared by the Thermal Syndicate (19).

§ 8.2 Solid and Liquid Elements

Aluminum: Rapid attack when molten (3, 19)

Cadmium: No reaction at 710° F (19). Attack by vapor (3).

Calcium: No attack at 1200° F (3).

Carbon: Reduction at 1920° F (3, 19).

^{1/}See § 8.20.

Gold: No attack (19).
 Lead: Very slight attack at 1830 ° F (21).
 Lithium: No attack at 550° F (3, 19).
 Magnesium: Rapid attack when molten (3, 19).
 Manganese: Slight reaction at high temperatures (19).
 Mercury: No attack (3, 19).
 Molybdenum: No attack (19).
 Phosphorus: Reacts (3, 19).
 Platinum: Very slight reaction (3, 19).
 Silicon: Reacts when molten (3, 19).
 Silver: No reaction (3, 19).
 Sodium: Rapid attack when molten (3, 19).
 Sulfur: Slight attack at 1830° F (3, 19, 20).
 Thallium: No reaction (19).
 Tin: No reaction (3, 19).
 Tungsten: No reaction at 4500° F (1).
 Zinc: No reaction (3, 19).

§ 8.3 Gases

Carbon Monoxide: No reaction (19).
 Chlorine: No attack even when wet and hot (3, 18, 19, 22).
 Fluorine: No attack when dry at 520° F. Rapid attack when wet (19).
 Hydrogen: Slight reaction at 1830° F (19).
 Hydrogen Chloride: No reaction (3).
 Sulfur Dioxide: No reaction (3).

§ 8.4 Oxides ^{1/}

In general: Basic oxides usually react above 1200° F and promote devitrification (17, 19).
 Aluminum: Slow reaction at 1830° F (19).
 Arsenic: Reacts (14).
 Barium: Reacts at 1650° F (3, 19).
 Cadmium: Reacts (19).
 Calcium: Reacts at 1650° F (3, 19).

^{1/}See also § 8.20.

Copper: Reacts at 1470° F (3, 13, 19).
 Gadolinium: Reacts at 2190° F (6).
 Iron: Slight attack at 1650° F (3, 19).
 Lanthanum: Reacts at 2190° F (6).
 Lead: Reacts when fused (19).
 Magnesium: Reacts at 1650° F (3, 19).
 Neodymium: Reacts at 2190° F (6).
 Praesodymium: Reacts at 2190° F (6).
 Tellurium: Reacts at 1400° F (19).
 Thorium: Eutectic at 3000° F (1).
 Vanadium: Causes devitrification at 1380° F (19).
 Ainc: Reacts at 1470° F (19).

§ 8.5 Fluorides

In general: May attack when molten. Bifluorides usually attack (19).
 Organic: React at about 1470° F (19).
 Ammonium: Attacks and causes devitrification at elevated temperatures (19).
 Potassium: Reacts when fused (19).
 Sodium-Calcium Mixture: Causes devitrification when fused (19).
 Zinc: Slight reaction at 400° F (19).

§ 8.6 Chlorides

Organic: No reaction (22).
 Barium: Attacks when Fused (19).
 Boron: No reaction at 1300° F (19).
 Copper: No reaction when fused (19).
 Lithium: Reacts and causes devitrification when fused (19).
 Mercury: No reaction at 660° F (19).
 Platinum-Ammonium: No reaction at 1650° F (19).
 Potassium: Causes devitrification (19).
 Silicon: Probable attack (19).
 Sodium: No reaction at 930° F. Attacks and causes devitrification at 1290° F (19).
 Sodium-Potassium-Aluminum Mixture: Attacks when fused (19).
 Zinc: No attack at 750° F (19).

§ 8.7 Iodides

Barium: Attacks at elevated temperatures (19).

Cesium: No attack at 1200° F (19).

Strontium: No attack (19).

§ 8.8 Sulfides

Hydrogen: Slight reaction at 1830° F (19).

Zinc: Reacts (19).

§ 8.9 Cyanides

Sodium: Slight reaction in concentrated aqueous solution (19).

§ 8.10 Borates

In general: Attack when fused (19).

Zinc: Reacts at 1110° F (19).

§ 8.11 Carbonates

Sodium: Reacts in concentrated aqueous solution or fused. Under high pressure, aqueous solution causes devitrification at 750° F. (3, 9, 15, 19).

Sodium-Lithium Mixture: Reacts at 1090° F (19).

§ 8.12 Chromates

Lead: Reacts at 1020° F (19).

Zinc: No attack at 1830° F (19).

§ 8.13 Nitrates

In general: No attack (19).

Potassium: No attack (19).

Sodium: No attack (19).

Strontium: Reacts when fused (19).

§ 8.14 Phosphates

In general: React when fused (19).

Lithium: Reacts when fused (19).
 Magnesium-Ammonium: No reaction during dehydration (19).
 Potassium: Reacts (19).
 Sodium: Reacts (19).
 Sodium Bi-: No reaction (3).
 Zinc: Slight reaction at 390° F (19).

§ 8.15 Sulfates

In general: No attack (19).
 Barium: Attack at 1120° F (19).
 Lead: No attack at 1020° F (19).
 Lithium: Reacts at 1830° F (19).
 Magnesium: No reaction at 1560° F (19).
 Manganese: No reaction at 1380° F (19).
 Sodium: No reaction (19).
 Sodium-Magnesium Mixture: Slight reaction at 1650° F (19).

§ 8.16 Hydroxides

Ammonium: Reacts at high temperatures (3).
 Barium: Slight reaction (3, 16)
 Potassium: Reacts (3).
 Sodium: Reacts (3, 9, 10, 15, 19).
 Strontium: Reacts (16).

§ 8.17 Acids

Organic: No attack (3).
 Acetic: No attack at 1110° F (19).
 Arsenic: No reaction (19).
 Hydrochloric: Slight reaction at elevated temperatures (3, 15).
 Hydrofluoric: Rapid attack (3).
 Nitric: No attack (3).
 Phosphoric: Slight reaction below 570° F when concentrated (3, 5, 19).
 Sulfuric: No attack at 5000 psi and 750° F (3, 24).

§ 8.18 Water

No attack at ordinary pressures and temperatures. Less than 0.2 per cent solubility up to 7000 psi and 850° F (11, 12, 19, 23).

§ 8.19 Miscellaneous

Lead Selenide: No reaction at 230° F (19).

Lead Telluride: No reaction at 1740° F (19).

Sodium Tungstate: Causes devitrification (19).

Thallium-Mercury Alloys: Attacks (19).

§ 8.20 Prediction of Reactions

Thermochemical calculations can provide some indication of reaction probability in the absence of experimental data. In general, a free energy change of about 2 to -5 kcal per mole of oxygen in the reaction indicates a possible reaction, probably at a slow rate. With increasingly negative free energy change, the probability of reaction increases and the possibility of a high reaction rate is greater.

The reliability of predictions drawn from free energy calculations is likely to be better for higher temperatures since the activation energy barrier is more likely to be overcome with greater atom mobility. In any event, thermochemical calculations are likely to yield conservative predictions. A reaction with a low negative or positive free energy change will rarely prove to occur at a rapid rate, even at temperatures of the order of 2000° F.

Collections of thermochemical data which are useful for such calculations have been published under a JANAF effort (2), by Glassner (4), and by Kubaschewski and Evans (7).

Useful information concerning attack of fused silica by ceramic materials is available from phase diagrams which have been developed for use in glass engineering. The possibility of attack is indicated by the presence of a eutectic or other low temperature invariant point. One good compilation of such diagrams is in common use in the ceramic industry (8).

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CHAPTER IX

OTHER PROPERTIES

- § 9.1 Introduction
- § 9.2 Resistivity
- § 9.3 Dielectric Properties
- § 9.4 Optical Properties
- § 9.5 References for Chapter IX

§ 9.1 Introduction

The properties of fused silica which pertain to structural uses have been treated in the preceeding chapters. In this chapter, very brief summaries are given of two remaining groups of data, electrical and optical. The structural engineer should not have frequent need for such data and their tabulation is abbreviated as a result. In cases of special need, the references cited should serve as guides to more extensive information in the literature.

Very good compilations of optical data are available from the manufacturers listed in Chapter XI. The engineer who deals more than casually with optical applications should obtain these compilations since optical properties depend much more strongly on the method of manufacture than do any of the structural properties.

§ 9.2 Resistivity

Fused silica of high purity does not display electronic conductance, hence does not obey Ohm's law (2). The presence of very small concentrations of impurities, of the order of hundredths of a per cent or less, lower the resistivity several orders of magnitude (5). Ionic conduction by these impurities, usually sodium, accounts for the electrical energy flow.

As a result of the strong dependence of the resistivity on impurity level, published values of the electrical resistivity differ rather widely (9, 10, 11). Owen and Douglas found up to three orders of magnitude difference in the resistivity in different grades of fused silica from the same manufacturer (8).

The values for Figure 6 were taken from the work of Veltri (11) and

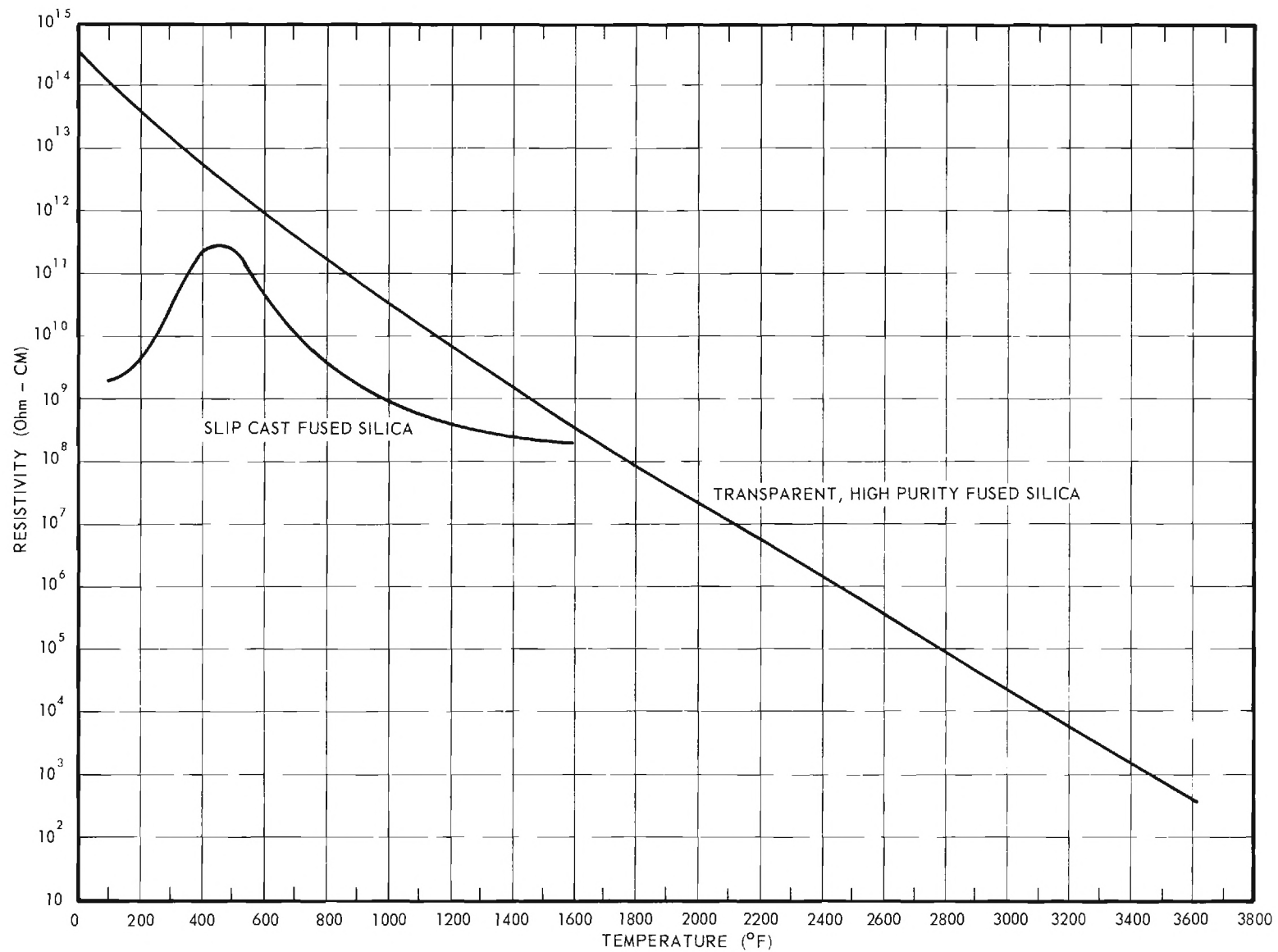


Figure 46. Electrical Resistivity of Fused Silica.

Pentecost (10), both of whom worked with high purity material.

Since small differences in impurity content result in large differences in the electrical conductivity, fused silica from different manufacturers will vary greatly from the resistivity given in Figure 46. If the resistivity is critically important, the manufacturer should be consulted for information concerning the grade to be used. In comparing different grades, the sodium content is usually controlling. Owen and Douglas found an exponential decrease in electrical resistivity with sodium content over the range from 0.1 to 10 ppm (8).

The electrical resistivity of slip-cast fused silica is lower at low temperatures than that of glass-worked fused silica of comparable purity. Since the resistivity is nearly that of the glass-worked forms at higher temperatures, the low value at low temperatures can probably be ascribed to adsorbed water vapor on the surfaces of the pores which is evolved as the specimen is heated. A typical curve for slip-cast fused silica is shown in Figure 46 (13).

§ 9.3 Dielectric Properties

While the resistivity of fused silica is strongly dependent on the impurity content, the dielectric properties are not. Instead, the dielectric constant and loss tangent are controlled almost entirely by the water content 1/ (8). Materials which are electrically fused tend to have a lower water content 2/ than flame fused and synthetic fused silica. A lower water content results in a lower dielectric constant and a higher loss tangent.

At room temperature, the dielectric constant is independent of frequency over the range from 10^2 to 2.5×10^{10} cps (12). The room temperature loss tangent varies somewhat with frequency, ranging from about 8×10^{-4} at 10^2 cps to a low of about 10^{-4} at 10^{10} cps. This variation depends strongly on the manufacturing process used to prepare the fused silica (12).

The temperature dependence of both the dielectric constant and loss tangent depends on the frequency. At frequencies below 10^4 cps, the

1/See § 2.13.

2/See Table VII, § 4.8.

dielectric constant does not change up to about 400° F (12) but at higher temperatures, strong changes occur. Below 10^4 cps, the loss tangent varies over several orders of magnitude as the temperature increases (12). The variation in dielectric constant with temperature becomes very much smaller above 10^4 cps (8) and the loss tangent is reasonably stable at 10^{10} cps (12).

The dielectric constant and loss tangent for electrically fused silica (12) and slip-cast fused silica (14) at 10^{10} cps are shown in Figures 47 and 48.

§ 9.4 Optical Properties

In the wave-length range from about 0.3 to about 1 micron, the optical transmittance of transparent fused silica is essentially independent of its source, varying from about 90 to 98 per cent over a 1 cm. path for all types. In the infrared region, vast differences are observed in the transmittance depending on the water content 1/. A characteristic absorption band appears at 2.73 microns, where the transmittance varies from almost 0 for "wet" fused silica to about 90 per cent for "dry" fused silica (6).

Fused silica usually shows a strong absorption band in the ultraviolet region at 0.24 microns. This absorption is due to an oxygen deficiency 2/ and can be increased by heating in a reducing atmosphere (4) or decreased by heating in an oxidizing atmosphere or in a vacuum (1). In commercial grades of transparent fused silica, the stoichiometry varies widely enough to result in a transmittance for a 1 cm. path length varying from less than 30 to more than 95 per cent at 0.18 microns (6).

The transmittance of fused silica between 40 and 100 microns is essentially zero (3). In the very long wave-length infrared region from about 100 to 200 microns, the transmittance again increases.

The refractive index of fused silica is relatively constant over the visible light range. From 0.35 to 3.51 microns, the refractive index varies from 1.47752 to 1.40570 (7).

As discussed above, the optical properties of fused silica vary greatly

1/See § 2.13, Table VII § 4.8.

2/See § 2.12.

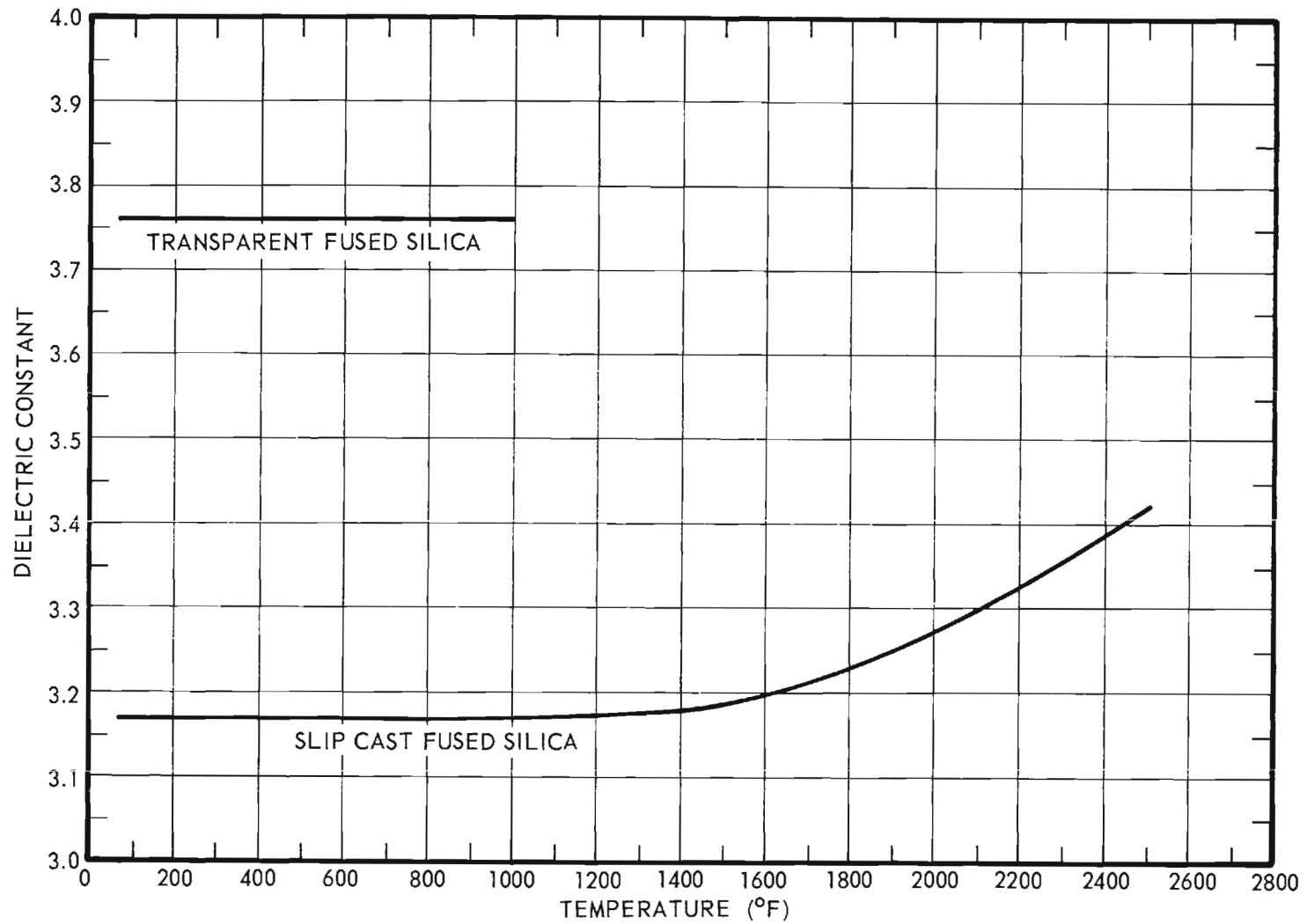


Figure 47. Dielectric Constant of Fused Silica.

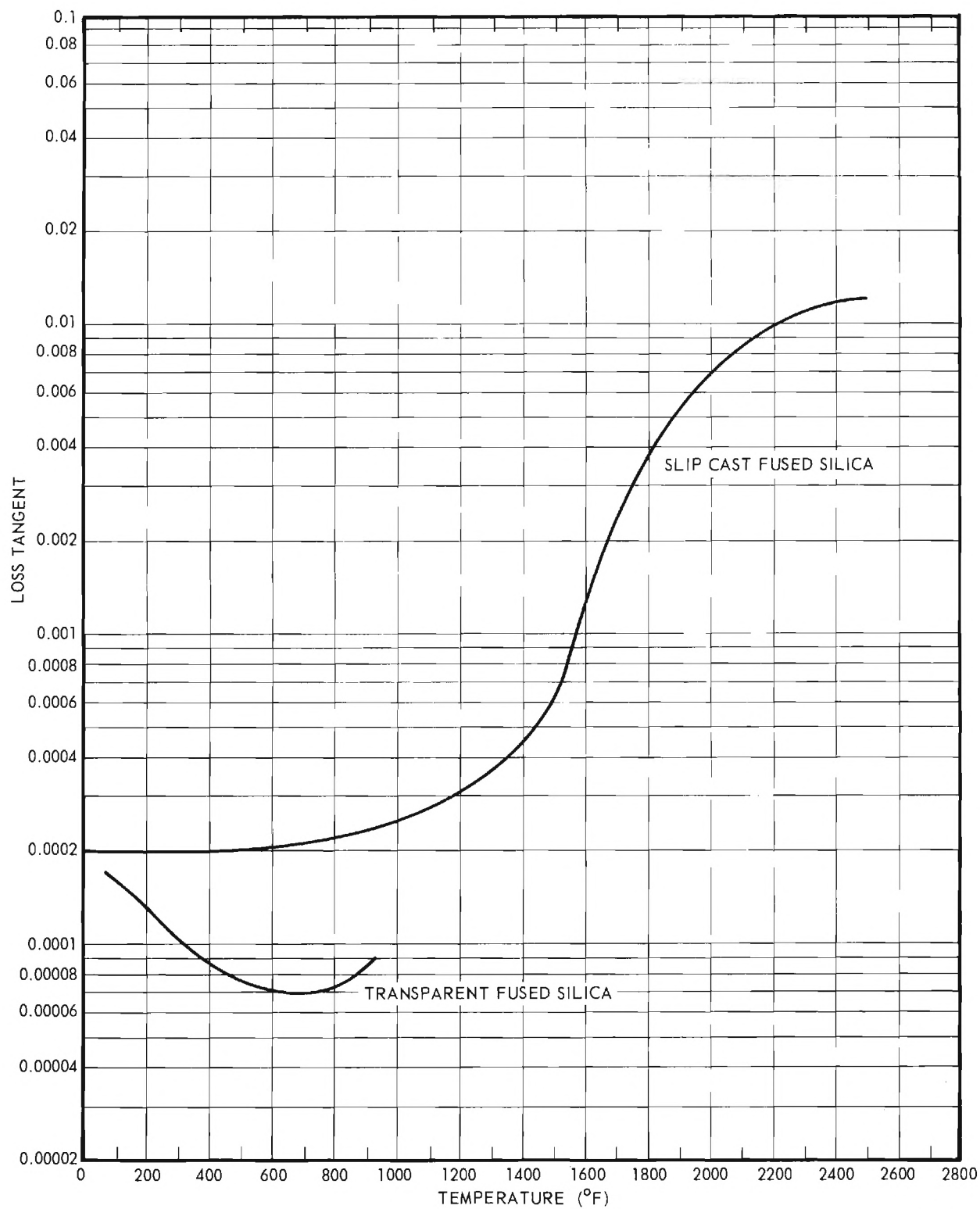


Figure 48. Loss Tangent of Fused Silica at 10^{10} cps.

in the infrared and ultraviolet region depending on the method of manufacture. Great efforts are constantly being made in industry to produce new materials for use in these regions and the manufacturers should be contacted if these properties are of importance.

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CHAPTER X

OTHER FORMS

§ 10.1 Introduction

§ 10.2 Fibers

§ 10.3 Foam

§ 10.4 References for Chapter X

§ 10.1 Introduction

In addition to the dense forms of fused silica, discussed in the preceeding chapters, other forms are used in some applications. These forms consist of either fibers or low density foam. While fibrous and foamed fused silica are not, strictly speaking, structural forms, they may have occasional structural uses and the design engineer should be aware of their availability.

Unfortunately, little is available in the literature concerning these less common forms of fused silica. Their structure independent properties will be similar to those of the dense forms but other properties vary greatly. In this chapter, a brief summary is given of some of the information on structure dependent properties which is currently available.

§ 10.2 Fibers

Fused silica was formed into fibers as early as 1887. A most interesting review of the early fabrication methods was published by Frost (6). An extensive survey was made of the properties and uses of fused silica fibers by Tighe (11).

The strength of fused silica fibers is discussed in a previous chapter 1/. The other properties of the fibers themselves should be much the same as those of transparent fused silica.

Fibers are used most often in the form of springs (1, 10), because of their excellent elasticity, strength, and refractory character, or as felted insulation (5, 9). In the latter form, the thermal conductivity is of the order of 0.02 Btu/hr ft ° F at 300° F and 0.08 Btu/hr ft ° F at 1000° F (7).

1/See § 4.2.

§ 10.3 Foam

Two types of fused silica foam are commercially available. Closed-pore, glassy foam is prepared by carbonaceous foaming of a silica melt 1/. Open-pore foam is prepared by organic foaming of a fused silica slip at room temperature, followed by drying and firing 2/. The walls of the pores in the slip-foam consist of small particles which sinter much as in ordinary slip-cast fused silica.

As a result of their different structures, the two types of foam differ appreciably in properties. The most noticeable differences in service are that the glassy foam can contain liquids and gases while the slip-foam cannot and that the slip-foam does not lose its integrity upon devitrification while the glassy foam is seriously damaged.

The physical properties of fused silica foam are given in Table X 3/.

Foamed fused silica has been considered as a dielectric material (8). Glassy foam with a density of 46.4 lb/ft³ was found to have a volume resistivity of approximately 10¹⁶ ohm-cm. at room temperature and 10⁶ ohm-cm. at 1830° F. Glassy foam with densities ranging from 17.4 to 46.4 lb/ft³ showed a dielectric constant of 1.32 to 1.59 and a loss tangent of 5 x 10⁻⁴ to 1.3 x 10⁻³ at room temperature and 10¹⁰ cps. These properties did not vary consistently with density and were presumably governed by the undetermined impurity content of the experimental foams.

1/Pittsburg Corning Corporation.

2/Glasrock Products, Inc.

3/See also Note 2, p. 78.

TABLE X
PROPERTIES OF FUSED SILICA FOAMS

	<u>Foamsil 1/</u>	<u>No. 25 2/</u>	<u>No. 50 2/</u>
Density (lb/ft ³)	10-15	29	47
Open Porosity (%)	≈ 0	80	67
Modulus of Rupture (psi)	120-150	120	410
Compressive Strength (psi)			
Room Temperature	130-210	400	1250
2000° F	----	540	1050
Thermal Conductivity (Btu/hr ft °F)			
200° F	0.05	---	0.10 (Approx.)
500° F	0.08	---	0.10
1000° F	----	---	0.10
1500° F	----	---	0.12
2000° F	----	---	0.22

1/Pittsburgh Corning Corporation (2, 3, 4).

2/Glasrock Products, Inc. (12, 13).

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 12. Walton, J. D., "Fused Silica Ceramics," Ceramic Age 57 (May 1961).
- NOTE: The following references are to reports issued under this contract.
See Appendix B for complete listing.
13. Quarterly Report No. 6, p. 4.

CHAPTER XI

APPLICATIONS AND MANUFACTURERS

- § 11.1 Introduction
- § 11.2 Chemical Industry
- § 11.3 Metallurgical Industry
- § 11.4 Glass Production
- § 11.5 Aero- and Astronautics
- § 11.6 Nuclear Engineering
- § 11.7 Commercial Index
- § 11.8 References for Chapter XI

§ 11.1 Introduction

In this chapter, very brief mention is made of the literature describing more novel structural uses of fused silica. This is not meant to represent even a small cross section of the potential or actual uses which are too numerous even to be summarized. The manufacturers listed in the final section can provide a vast amount of information in any particular area of interest.

§ 11.2 Chemical Industry

Many unusual applications of fused silica in the chemical industry are illustrated in the booklet "About Vitreosil" published by the Thermal Syndicate (11). This booklet is profusely illustrated and is most interesting.

§ 11.3 Metallurgical Industry

Fused silica is used in precision casting (1, 5, 7, 8) and in precision brazing and heat treating (2, 12). The latter application is possibly representative of the largest shapes of fused silica which have been precision shaped.

§ 11.4 Glass Production

In Europe and Russia, large blocks of fused silica are used for several purposes in glass-making tanks (9, 10). In these applications, fused silica is superior to the more conventional materials although attack by the alkaline melt does occur.

§ 11.5 Aero- and Astronautics

Fused silica is receiving widespread attention in applications pertaining to high speed flight vehicles. At the present time, it is a leading candidate for use in radomes. These applications were extensively reviewed by Walton (13, 14).

§ 11.6 Nuclear Engineering

Fused silica is used in several reactor applications in Europe (3, 4). It has been examined for use as a plasma containment vessel and suffered no damage under conditions which no other material tested survived (6).

§ 11.7 Commercial Index

The following list comprises the majority of firms dealing with fused silica in the United States. The list is not complete and firms may be erroneously included or omitted. In particular, no foreign firms were listed which do not have subsidiary companies or distributors in the United States.

A. Glass-worked products

1. Avins Industrial Products Corporation
47 New Street
New York 4, New York
(Distributor for No. 26)
2. Bausch and Lomb, Inc.
98463 Bausch Street
Rochester 2, New York
(Fabricator of optical components)
3. P. W. Blackburn, Inc.
69 Main Street
Dobbs Ferry, New York
(Distributor)
4. Boxtton-Beel, Inc.
37 Richardson
Brooklyn, New York
(Fabricator of optical components)
5. The Carborundum Company
P. O. Box 268
Perth Amboy, New Jersey
(Silicon nitride bonded fused silica)

6. Corning Glass Works
1946 Crystal
Corning, New York
(All phases)
7. Dynasil Corporation
Box D
Berlin, New Jersey
(High purity fused silica)
8. Englehard Industries, Inc.
Amersil Quartz Division
685 Ramsey Avenue
Hillside, New Jersey
(All phases)
9. Esco Products, Inc.
49 Oak Ridge Road
Oak Ridge, New Jersey
(Fabricator)
10. Garner Glass Company
177 S. Indian Hill Blvd.
Claremont, California
(Fabricator)
11. General Electric Company
1 River Road
Schenectady, New York
(All phases)
12. Johns-Manville
22 E. 40th Street
New York 16, New York
(Felted insulation only)
13. Kaufman Glass Company
1209-21 French Street
Wilmington, Delaware
(Distributor)
14. Hugo P. Keller, Jr.
50 E. 42nd Street
New York, New York
(Limited fabrication)
15. Kontes Glass Company
Vineland, New Jersey
(Fabricator)
16. Owens-Illinois Glass Company
P. O. Box 1035
Toledo 1, Ohio
(Special products only)

17. Precision Glass Products Company
6140 Beechwood
Philadelphia, Pennsylvania
(Fabricator)
18. Quartz et Silice
8 Rue D' Anjou
Paris 8, France
(All phases)
19. Quartz Products Corporation
P. O. Box 628
Plainfield, New Jersey
(Subsidiary of No. 18).
20. Silk City Ceramics and Tool Manufacturing, Inc.
221 Seventh Avenue
Hawthorne, New Jersey
(Fabricator)
21. Solar Silica Corporation
P. O. Box 4-T
Pompton Lakes, New Jersey
(Manufacture translucent fused silica, principally for own use.)
22. Thermal Syndicate Ltd.
P. O. Box No. 6
Wallsend Northumberland,
England
(All phases)
23. Thermal American Fused Quartz Company, Inc.
Rt. 202 and Change Bridge Road
Montville, New Jersey
(Subsidiary of No. 22)
24. Valpey Crystal Corporation
1200 Highland Avenue
Holliston, Massachusetts
(Fabricator of optical elements)
25. Wacom Corporation
15 William Street
New York 5, New York
(Distributor)
26. Westdeutsche Quartz Schmelze, G.M.b.H.,
Geesthacht/Elbe
Germany

B. Slip-Casting Products

1. Ceram, Inc.
P. O. Box 12347
Atlanta, 5, Georgia
(Slip, grain, cement)

2. Glasrock Products, Inc.
1101 Glidden Street
Atlanta, Georgia
(Slip, grain, cement)

§ 11.8 References for Chapter XI

1. Anon., "Glascast Molds for Precision Casting of High Temperature Alloys," Ind. Heating 23 [1] 140 (1956).
2. Anon., "New Refractory Material Offers Spectacular High Temperature Performance," Brick Clay Rec. 137 [6] 58 (1960).
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6. Dugdale, R. A., et al, "Some Effects of Thermal Shock Produced by Intense Gas Discharges," Trans. Brit. Ceram. Soc. 60 427 (1961).
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11. The Thermal Syndicate, Ltd., "About Vitreosil," P. O. Box 6, Wallsend, Northumberland, England (1958).
12. Walton, J. D., "Fused Silica Ceramics," Ceramic Age 57 (May 1961).
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14. Walton, J. D., and N. E. Poulos, "Slip-Cast Fused Silica," Special Report No. 43, p. 26, Georgia Institute of Technology (1964).

APPENDIX

APPENDIX A

PERSONNEL

Major contributing personnel in the performance of this contract were:

Boland, Paul	Research Assistant
Bomar, S. H.	Research Assistant
Colcord, A. R.	Assistant Research Engineer
Fleming, J. D.	Research Engineer
Fuller, S. H.	Research Assistant
Gross, D. I.	Research Assistant
Harris, J. N.	Assistant Research Engineer
Hearn, N. K.	Assistant Research Physicist
Hochman, R. F.	Associate Professor
Johnson, J. W.	Assistant Research Physicist
Koenig, J. H.	Assistant Research Physicist

APPENDIX B

PRIOR REPORTS

Previous reports issued under this contract are:

1. Monthly Letter Report Nos. 1 - 65, Issued each month since December 1958.
2. Progress Report No. 1, ORO-209, August 1959.
3. Progress Report No. 2, ORO-325, Part 1, August 1960.
4. Progress Report No. 2, ORO-325, Part 2, (Declassified), August 1960.
5. Progress Report No. 3, ORO-577, August 1961.
6. Quarterly Report No. 1, ORO-578, April 1962.
7. Summary Report No. 1, TID-17322, July 1962.
8. Quarterly Report No. 2, TID-17530, October 1962.
9. Quarterly Report No. 3, TID-18286, January 1963.
10. Quarterly Report No. 4, TID-18891, April 1963.
11. Summary Report No. 2, TID-19057, June 1963.
12. Quarterly Report No. 5, TID-20026, October 1963.
13. Quarterly Report No. 6, TID-20589, January 1964.

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Dr. Louis Baker
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Lockheed-Georgia Company
Div. of Lockheed Aircraft Corp.
Marietta, Georgia
Attn: Charles K. Bauer, Manager
Scientific and Technical Information
Department

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Metals and Ceramics Division
Oak Ridge National Laboratory
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Oak Ridge, Tennessee

Mr. Robert E. Cowan
Ceramics Section, CMB-6
Los Alamos Scientific Laboratory
Post Office Box 1663
Los Alamos, New Mexico

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Reactor Physics and Engineering
Phillips Petroleum Company
Post Office Box 2067
Idaho Falls, Idaho

Mr. J. Elston
Department de Metallurgie
Commissariat a L'Energie Atomique
Centre d'Etudes Nucleaires de Saclay
Boite Postals No. 2
Saclay, France

Dr. E. A. Evans
Ceramics Research and Development Operation
Hanford Atomic Products Operation
Richland, Washington

Dr. Arthur W. Flynn
Ebasco Services, Inc.
2 Rector Street
New York 6, New York

Dr. John H. Frye, Director
Metals and Ceramics Division
Oak Ridge National Laboratory
Post Office Box X
Oak Ridge, Tennessee

Mr. R. H. Gordon
Ebasco Services, Inc.
2 Rector Street
New York 6, New York

Dr. David H. Gurinsky, Head
Metallurgy Division
Brookhaven National Laboratory
Upton, L. I., New York

Dr. J. Hammond
Metals and Ceramics Division
Oak Ridge National Laboratory
Post Office Box X
Oak Ridge, Tennessee

DISTRIBUTION LIST (Concluded)

Mr. A. H. Lazar
Babcock and Wilcox Company
1201 Kemper Street
Lynchburg, Virginia

Mr. C. F. Leitten
Metals and Ceramics Division
Oak Ridge National Laboratory
Post Office Box X
Oak Ridge, Tennessee

Mr. William J. O'Leary
Allis-Chalmers Manufacturing Company
508 Kennedy Street, N. W.
Washington 11, D. C.

Mr. George Robinson
Babcock and Wilcox Company
1201 Kemper Street
Lynchburg, Virginia

Mr. M. Salesse
Chief, Department of Metallurgy
Commissariat A L'energie Atomique
Centre D'etudes Nucleaires De Saclay
Boite Postale No. 2
Gif Sur-Yvette (Seine-et-Oise)
France

Dr. E. E. Sinclair
Division of Reactor Development
U. S. Atomic Energy Commission
Washington 25, D. C.

Mr. Samuel Sklarew
The Marquardt Corporation
16555 Saticoy Street
Van Nuys, California

Mr. D. E. Williams, Director
Reactor Division
Idaho Operations Office
U. S. Atomic Energy Commission
Idaho Falls, Idaho

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CONVERSION FACTORS

<u>To Convert</u>	<u>To</u>	<u>Multiply By</u>
atmospheres	kg/cm ²	1.0333
atmospheres	mm. mercury	760.0
bars	lb/in ²	14.50
bars	kg/m ²	1.020 x 10 ⁴
Btu	cal.	252.0
Btu/hr	cal/sec	0.0700
Btu/hr	watts	0.2931
Btu/hr ft °F	cal./sec.cm. °C	4.134 x 10 ⁻³
Btu/hr ft °F	watts/cm °C	0.01731
Btu/lb.	cal./gm.	0.5556
Btu/lb. °F	cal./gm. °C	1.000
ft ³	liters	28.32
feet	meters	0.3048
gallons	liters	3.785
inches	cm.	2.540
in. ²	cm. ²	6.452
lb.	kg.	0.4536
lb/ft. ³	gm./cc.	0.01602
lb/in. ² (psi)	kg./m. ²	703.1

38
125

26