GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT INITIATION

Date: October 29, 1973

Project Title: Aggregate Casting Techniques for Producing High Density Slip-Cast Fused Silica Radomes.
Project No.: A-1572
Project Director: Mr. J. N. Harris
Sponsor: U.S. Army Missile Command; Redstone Arsenal, Alabama
Effective: October 4, 1973
Estimated to run until: June 4, 1974*

Type Agreement: DAAH01-74-C-0210
Amount: $29,031.00

*Includes 2 months for preparation and distribution of Final Report.


Technical Matters

Sponsor Contact Persons: (Individual not named)
Chief, Materials Function
Ground Equipment and Materials Directorate
U.S. Army Missile Command
ATTN: AMSMI-RLM
Redstone Arsenal, Ala. 35809

Contractual Matters (thru GTRI)
Mr. R. J. Whitcomb (ACO)
ONRRR Campus


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GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT TERMINATION

Nov. 21, 1974

Date

PROJECT TITLE: Aggregate Casting Techniques for Producing High Density Slip-Cast Fused Silica Radomes

PROJECT NO: A-1572

PROJECT DIRECTOR: Mr. J. M. Harris

SPONSORS: U. S. Army Missile Command; Redstone Arsenal, Ala.

TERMINATION EFFECTIVE: June 4, 1974

CHARGES SHOULD CLEAR ACCOUNTING BY: Oct. 31, 1974

CLOSEOUT ITEMS REMAINING:
1. Final Report of Inventions
2. Government Property Inventory & Related Certificate
3. Classified Material Certificate

HIGH TEMPERATURE MATERIALS DIVISION

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Project File
Sue Corbin
Commanding General
U. S. Army Missile Command
Attention: AMSMI-RLM
Redstone Arsenal, Alabama 35809


Gentlemen:

Under the Georgia Tech Engineering Experiment Station accounting system, the information required for this report is sometimes unavailable until the 15th day of the month following the close of the reporting period. Every effort will be made to comply with the reporting date of the 8th of each month, but in some months this may not be possible.

a. Man-hours

The man-hours expended during the month of October was 11.9. Percent of total man hours expended 6. The reason for the low total man hours was the time to obtain necessary materials and supplies needed to begin extensive laboratory work. The remaining hours are sufficient to complete the objectives of this contract.

b. Total Funds Expended

Total funds expended as of 31 October 1973 were $1,759.30, of this amount $191.67 was for materials and supplies and the remainder was for Personal Services and Overhead. Retirement charges at 8.5 percent of Personal services have not been posted and are not included in the above total. The percentage of total funds expended to date is 6 percent. Remaining funds are adequate to complete the objectives of this contract.

c. Work Completion

Estimates of percent of work completed as of the end of the first reporting period is 6 percent.

Respectfully submitted,

Joe N. Harris
Project Director
Commanding General  
U. S. Army Missle Command  
Attention: AMSMI-RIM  
Redstone Arsenal, Alabama  35809


Gentlemen:

Cost and Performance Report No. 1 contained a typographical error. The man hours expended for October should have read 122.5 instead of 11.9. The rest of the information in Report No. 1 is correct as stated.

   a. Man-hours

      The man-hours expended during the month of November was 258.2. Percent of total man hours expended 19.1. The remaining hours are sufficient to complete the objectives of this contract.

   b. Total Funds Expended

      Total funds expended or encumbered as of 30 November 1973 were $5,670.03, of this amount $793.41 was for materials and supplies and the remainder was for Personal Services, Overhead and Retirement. Retirement charges at 8.5 percent of Personal services for the month of November have not been posted and are not included in the above total. The percentage of total funds expended to date is 19.5 percent. Remaining funds are adequate to complete the objectives of this contract.

   c. Work Completion

      Estimates of percent of work completed as of the end of this reporting period is 19 percent.

      Respectfully submitted,

   /s/ Joe N. Harris  
   Project Director

jw
January 8, 1974

Commanding General
U. S. Army Missile Command
Attention: AMSMI-RIM
Redstone Arsenal, Alabama 35809


Gentlemen:

a. Man-hours

The man-hours expended during the month of November was 195.4. Percent of total man hours expended 28.9. The remaining hours are sufficient to complete the objectives of this contract.

b. Total Funds Expended

Total funds expended or encumbered as of 31 December 1973 were $9,124.84, of this amount $793.41 was for materials and supplies and the remainder was for Personal Services, Overhead and Retirement. Retirement charges at 8.5 percent of Personal services for the month of December have not been posted and are not included in the above total. The percentage of total funds expended to date is 31.4 percent. Remaining funds are adequate to complete the objectives of this contract.

c. Work Completion

Estimates of percent of work completed as of the end of this reporting period is 29 percent.

Respectfully submitted,

Joe N. Harris
Project Director

jw
February 8, 1974

Commanding General
U. S. Army Missile Command
Attention: AMSMI-RLM
Redstone Arsenal, Alabama 35809


Gentlemen:

a. Man-Hours

The man-hours expended during the month of January was 284. Percent of total man hours expended 43.2. The remaining hours are sufficient to complete the objectives of this contract.

b. Total Funds Expended

Total funds expended or encumbered as of 31 January 1974 were $12,699.56, of this amount $915.32 was for materials and supplies and the remainder was for Personal Services, Overhead and Retirement. Retirement charges at 8.5 percent of Personal Services for the month of January have not been posted and are not included in the above total. The percentage of total funds expended to date is 43.7 percent. Remaining funds are adequate to complete the objectives of this contract.

c. Work Completion

Estimates of percent of work completed as of the end of this reporting period is 43 percent.

Respectfully submitted,

Joe N. Harris
Project Director

jw
Commanding General
U. S. Army Missile Command
Attention: AMSMI-RLM
Redstone Arsenal, Alabama 35809


Gentlemen:

a. Man-Hours

The man-hours expended during the month of February was 166. Percent of total man hours expended 52. The remaining hours are sufficient to complete the objectives of this contract.

b. Total Funds Expended

Total funds expended or encumbered as of 28 February 1974 were $15,304.23, of this amount $864.56 was for materials and supplies and the remainder was for Personal Services, Overhead and Retirement. Retirement charges at 8.5 percent of Personal Services for the month of February have not been posted and are not included in the above total. The percentage of total funds expended to date is 52.7 percent. Remaining funds are adequate to complete the objectives of this contract.

c. Work Completion

Estimates of percent of work completed as of the end of this reporting period is 53 percent.

Respectfully submitted,

Joe N. Harris
Project Director
Commanding General  
U. S. Army Missile Command  
Attention: AMSMI-RLM  
Redstone Arsenal, Alabama 35809  


Gentlemen:

a. Man-Hours

The man-hours expended during the month of March was 240. Percent of total man-hours expended 64. The remaining hours are sufficient to complete the objectives of this contract.

b. Total Funds Expended

Total funds expended or encumbered as of 31 March 1974 were $18,525.64, of this amount $886.28 was for materials and supplies and the remainder was for Personal Services, Overhead and Retirement. Retirement charges at 8.5 percent of Personal Services for the month of March have not been posted and are not included in the above total. The percentage of total funds expended to date is 63.8 percent. Remaining funds are adequate to complete the objectives of this contract.

c. Work Completion

Estimates of percent of work completed as of the end of this reporting period is 64 percent.

Respectfully submitted,

Earle A. Welsh  
Research Engineer  

jw
Commanding General  
U. S. Army Missile Command  
Attention: AMSMI-RIM  
Redstone Arsenal, Alabama 35809


Gentlemen:

a. Man-Hours

The man-hours expended during the month of April was 183. Percent of total man hours expended 73. The remaining hours are sufficient to complete the objectives of this contract.

b. Total Funds Expended

Total funds expended or encumbered as of 30 April 1974, were $21,018.25, of this amount $902.00 was for materials and supplies and the remainder was for Personal Services, Overhead and Retirement. Retirement charges at 8.5 percent of Personal Services for the month of April have not been posted and are not included in the above total. The percentage of total funds expended to date is 72.4 percent. Remaining funds are adequate to complete the objectives of this contract.

c. Work Completion

Estimates of percent of work completed as of the end of this reporting period is 80 percent.

Respectfully submitted,

Joe N. Harris  
Project Director
Commanding General
U. S. Army Missile Command
Attention: AMSMI-RLM
Redstone Arsenal, Alabama 35809

Subject: Cost and Performance Report No. 8, Contract DA-AC01-74-0210
for the Period 1 May-31 May, Project A-1572

Gentlemen:

a. Man-Hours

The man-hours expended during the month of May was 361. Percent of
total man hours expended 91. The remaining hours are sufficient to
complete the objectives of this contract.

b. Total Funds Expended

Total funds expended or encumbered as of 31 May were $26214.97. Of
this amount $1785.73 was for materials and supplies and the remainder
was for Personal Services, Overhead, and Retirement. Retirement charges
at 8.5 per cent of Personal Services for the month of May are not in-
cluded in the above total. The percentage of total funds expended to
date is 90.3. Remaining funds are adequate to complete the objectives
of this contract.

c. Work Completion

Estimates of per cent of work completed as of the end of this reporting
period is 91 per cent.

Respectfully submitted,

Joe N. Harris
Project Director
Commanding General  
U. S. Army Missile Command  
Attention: AMSMI-RM  
Redstone Arsenal, Alabama 35809  


Gentlemen:  

a. Man-Hours  
The man-hours expended during the month of June was 162. Percent of total man-hours expended 99. The remaining hours are sufficient to complete the objectives of this contract and the final report.  

b. Total Funds Expended  
Total funds expended or encumbered as of 30 June were $28570.73. Of this amount $1814.03 was for materials and supplies and the remainder was for Personal Services, Overhead and Retirement. Retirement charges at 8.5 per cent of Personal Services for the month of June will be $113.81 and is not included in the above total. The percentage of total funds expended to date is 99. Remaining funds are adequate to complete the final report.  

c. Work Completion  
All work is completed with the exception of completion and submission of the final report.  

Respectfully submitted,  

Joe N. Harris  
Project Director  
js
Chief, Materials Function  
Ground Equipment and  
  Materials Directorate  
U. S. Army Missile Command  
Attn: AMSMI-RIM  
Redstone Arsenal, Alabama 35809  

Subject: Technical Progress Letter No. 1, Contract DA-AH01-74-0210  
  for the Period 4 October - 31 October 1973, Project A-1572  

Gentlemen:  

During the current report period, high purity fused silica cullet, technical  
  grade grain and slip were ordered. An extensive literature search was  
  carried out and a number of applicable references were found.  

During the next report interval, the technical grade slip and grain will  
  be characterized and initial studies of grain/slip mixtures will be  
  started.  

Respectfully submitted,  

Joe N. Harris  
Project Director  

jw
Chief, Materials Function  
Ground Equipment and Materials Directorate  
U. S. Army Missile Command  
Attn: AMSMIRIM  
Redstone Arsenal, Alabama 35809


Gentlemen:

Particle size distributions have been determined for the technical grade slip and a technical grade grain size fraction used in preliminary experiments as shown in Figures 1 and 2. The mean particle diameter of the slip is approximately six micrometers.

Pycnometer density determinations on size fractions of technical grade grain indicate that the grains contain significant amounts of closed porosity. These results are shown in Figure 3 as a plot of bulk density versus particle diameter. Density increases with decreasing grain size which suggests that excessively large grains contain voids and should not be used in technical grade compositions, if maximum densities are required. A check of both a technical grade slip and coarse (-10 +20 mesh) vitreous (high purity) silica grain indicates a particle density of approximately 2.2 grams per cc.

Compositions of 55 and 60 weight percent grain have been partially characterized as shown in Figure 4. The experimentally derived points approach the limiting packing efficiencies as defined by the lines joining the point labeled "theoretical maximum density" with the points corresponding to the grain and slip composition end members. Cast porosities in the range from 10 to 12 percent have been obtained. Normal slip-cast porosities are 15 to 16 percent.

During the next report period, compositions with 50 and 65 weight percent grain will be studied along with sintering rates for all compositions successfully cast.

Respectfully submitted,

Joe N. Harris  
Project Director

Enclosures
Figure 1. Particle Size Distributions for Technical Grade Fused Silica Slip.
Figure 2. Particle Size Distribution for -10 +20 Mesh Technical Grade Fused Silica Grain.
Figure 3. Bulk Density versus Particle Diameter for Technical Grade Fused Silica Grain.
Figure 4. Packing Diagram for Mixture of Slip and Grain Showing Composition with Theoretical Maximum Density and Experimentally Determined Packing Parameters and Compositions.
January 10, 1974

Chief, Materials Function  
Ground Equipment and Materials Directorate  
U. S. Army Missile Command  
Attn: AMSMIRLM  
Redstone Arsenal, Alabama  35809


Gentlemen:

During the current report period, work continued on characterizing the packing characteristics of the fused silica slip/grain system. The highest cast density (measured on samples bisque fired at 1500°F) has been 1.955 gm/cm³ for a 50/50 grain/slip composition. The samples for this composition are currently being sintered for modulus of rupture data. The highest modulus of rupture obtained is an average of 1370 psi for a 55/45 grain/slip composition by weight. The sintering rates and low modulus of rupture values are indicative of the low specific surface of the castings. It is expected that normal strength values will be obtained with the more highly reactive high purity slip/high purity grain system.

During the next report period, characterization of the grain/slip system will continue. It is expected that the high purity cullet will arrive during this period and that production of high purity grain will begin.

Respectfully submitted,

Joe N. Harris  
Project Director
February 13, 1974

Chief, Materials Function
Ground Equipment
and Materials Directorate
U.S. Army Missile Command
ATTN: AMSMI-RLM
Redstone Arsenal, Alabama 35809

Subject: Technical Progress Letter No. 4 for the Period 1 January 1974 -

Gentlemen:

At the request of Mr. Phillip A. Ormsby, Technical Monitor for this
program, this report is somewhat broader in scope than usual. It summa-
rizes all work performed to date, and includes a brief discussion of
anticipated difficulties and possible future work, along with a brief out-
line of the remainder of the program.

1. Current Report Period

During the current report period, work has been concentrated on
grinding and screening GE 204 fused silica cullet to obtain -10 +20 mesh
grain suitable for aggregate casting. After a brief study to optimize
grinding, grain is now being produced on a continuing basis. To date
approximately five kilograms of -10 +20 mesh material has been produced
along with an equal amount of -20 mesh fines.

2. Summary of Work to Date

Compositions of technical grade fused silica grain and technical grade
fused silica slip have been examined. The compositions consisted of the
following weight ratios of grain to slip: 65/35, 60/40, 55/45, 50/50,
45/55. The two extreme compositions were unusable. The 65/35 mixture did
not contain enough slip to fill the interstices between aggregate grains
and were too dry to flow into the mold. Water additions allowed flow, but
created extreme segregation, with the slip accumulating in the lower
portions of the sample. At the other extreme, the 45/55 mixture had an
excess of slip and produced samples with preferential settling of the grain
to the lower portions of the samples. The tendency towards segregation
limits compositions to a fairly narrow range.

The bulk densities of castings containing -10 +20 mesh grain are plotted
in Figure 1 as a function of weight percent fine component from slip. These
numbers do not correspond directly to those mentioned above since they have
been corrected for the water content of the slip. The solid line represents the maximum density obtainable for each composition. This represents a perfect mixture of two components whose size ratio approaches infinity. The small circles represent test samples made with -20 +50 mesh grain. The lower bulk density is due to the smaller difference in particle diameter between the slip and grain.

Firing studies have been made on all of these compositions. Figure 2 shows modulus of rupture versus composition for the samples. It appears that the large grains do not participate in sintering and that strength is proportional to the slip content.

To examine this more closely a multiple linear regression was performed on data from 24 test bars. The modulus of rupture was evaluated as a function of volume fraction grain, casting bulk density, sintering time, sintered bulk density, sintered Young's Modulus, and percent change in bulk density on sintering (a factor related to the actual amount of sintering). The correlation coefficient matrix is shown in Table 1. The figures in parenthesis represent the probability of obtaining the corresponding correlation coefficient from a similar group of samples drawn from a random population. The figures in Table 1 bear out the strong negative correlation between grain content and modulus of rupture as with composites studied on an earlier program, it also appears that strength is more closely related to degree of sintering rather than sintered density, although the correlation may be somewhat forced as shown in Figure 3, a plot of sintering shrinkage versus modulus of rupture.

3. **Present and Anticipated Problem Areas**

At present the major problem area concerns obtaining higher strength from the aggregate castings. Since, as pointed out previously, the aggregate grains do not seem to be sintering, no further attempts to optimize technical grade compositions will be made. A test firing at 2300°F showed that the necessary densification could be obtained but with technical grade material, the added sintering is accompanied by devitrification which lowers strength. This is not expected to present problems with the much more reactive high purity materials.

A related anticipated problem area is that of obtaining high strength at a reasonable density. Since castings can easily be made with bulk densities higher than those found in normal sintered hardware, i.e., around 1.96 gm/cm³, the casting sintered to high strength will be approaching densities where all porosity will be closed pore. At these densities the threshold for rain erosion damage will be higher, but the lack of connected porosity might result in catastrophic failure once the threshold is exceeded. This problem will be solved by using lower density castings, perhaps containing a finer aggregate. This type of composition should retain all of the advantages of aggregate casting, such as reduced casting time and drying shrinkage, while allowing production of sintered hardware comparable to high purity slip cast fused silica.
4. **Projected Work**

The remainder of the experimental program will be devoted to development of high purity aggregate castings. Four final compositions with fired densities ranging from approximately 1.92 gm/cc to whatever maximum density can be obtained will be compared with high purity slip cast fused silica. Tests to be conducted are room temperature and hot modulus of rupture (including elevated temperature creep testing), modulus of elasticity, and room temperature dielectric properties.

If these properties appear promising, two Sparrow size radomes will be cast from two of the compositions to determine shrinkage and drying properties. The radomes will then be sintered and checked for the degree of warpage or slumping present, for concentricity, total indicated run out and wall thickness variations.

A milestone forecast chart for the program is attached. Although the time for preparation of high purity aggregate has slipped due to late delivery of cullet from the vendor, it is expected that the remaining milestones can be met.

Respectfully submitted,

J. N. Harris  
Project Director
Table 1. Correlation Coefficient Matrix for Sintering Studies

<table>
<thead>
<tr>
<th></th>
<th>Dry Bulk Density</th>
<th>Sintering Time</th>
<th>Sintered Bulk Density</th>
<th>Sintered Young’s Modulus</th>
<th>% Change in Bulk Density</th>
<th>Modulus of Rupture</th>
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<tr>
<td>Volume Fraction</td>
<td>0.7013 (&lt;.001)</td>
<td>0.0727 (NC)</td>
<td>-0.0278 (NC)</td>
<td>-0.1492 (NC)</td>
<td>-0.9779 (&lt;.001)</td>
<td>-0.9648 (&lt;.001)</td>
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<td>Dry Bulk Density</td>
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<td>0.1608 (NC)</td>
<td>0.6797 (&lt;.001)</td>
<td>0.4341 (&lt;.05)</td>
<td>-0.6462 (&lt;.001)</td>
<td>-0.6047 (&lt;.005)</td>
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<td>Sintering Time</td>
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<td>0.2594 (NC)</td>
<td>0.4423 (&lt;.05)</td>
<td>0.0530 (NC)</td>
<td>0.0132 (NC)</td>
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<td>Sintered Bulk Density</td>
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<td>0.8017 (&lt;.001)</td>
<td>0.1205 (NC)</td>
<td>0.1538 (NC)</td>
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<td>Sintered Young’s Modulus</td>
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<td>--</td>
<td>0.2473 (NC)</td>
<td>0.2734 (NC)</td>
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<td>% Change in Bulk Density</td>
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<td>0.9787 (&lt;.001)</td>
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NOTES 1: Figures in parenthesis indicate probability of obtaining same degree of correlation from a sample of the same size drawn from a random population.

2: NC indicates non-significant correlation.
Figure 1. Bulk Density versus Weight Percent Fine Component for Aggregate Cast Fused Silica
Figure 2. Modulus of Rupture versus Percent Sintering Densification for Technical Grade Aggregate Cast Fused Silica and Slip Cast Fused Silica
Figure 3. Modulus of Rupture versus Weight Percent Fine Component for Aggregate Cast Fused Silica
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<th>Milestone Description</th>
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March 11, 1974

Chief, Materials Function  
Ground Equipment and Materials Directorate  
U. S. Army Missile Command  
Attention: AMSMI-RIM  
Redstone Arsenal, Alabama 35809


Gentlemen:

The greater portion of this month's effort was expended in producing more high purity fused silica aggregate. Sufficient supplies of both -10 +20, and -20 +50 mesh grain are now available to permit casting normal test samples. Sintering data has been collected by sintering high purity aggregate cast samples in a dilatometer, while heating at a constant rate of 220°C per hour. In this way densification rates over the range 1100-1350°C may be measured directly, and rates to 1500°C may be extrapolated with confidence. As expected sintering is at a greater rate than with comparable technical grade materials.

During the next report period a number of high purity aggregate cast compositions will be cast, sintered, and tested for flexural strength.

Respectfully submitted,

Joe N. Harris  
Project Director

jw
Chief, Materials Function  
Ground Equipment and Materials Directorate  
U. S. Army Missile Command  
Attn: AMSMI-RIM  
Redstone Arsenal, Alabama 35809


Gentlemen:

During the current report period, work has continued on the dilatometer sintering studies. The studies show, as expected, that sintering rates for slip-cast and aggregate cast materials are quite different. Sintering studies on high purity aggregate specimens have shown that there is an apparent maximum sintered density for castings at about 2.06 gm/cm$^3$. In addition, cursory modulus of rupture testing has indicated strengths up to about 2500 psi, a value far short of slip-cast material. Although high purity material is generally stronger than technical grade material, the results are still somewhat disappointing. It appears that the aggregate behaves as a large void and doesn't contribute to the mechanical strength of the casting.

During the current month, it is expected that remaining test work will be completed and that a draft final report will be prepared.

Respectfully submitted,

Earle A. Welsh  
Research Engineer

jw
May 10, 1974

Chief, Materials Function
Ground Equipment and Materials Directorate
U. S. Army Missile Command
Attn: AMSMI-RLM
Redstone Arsenal, Alabama 35809

Subject: Technical Progress Letter No. 7 for the Period 1 April-30 April 1974, Contract DA-AH01-74-C-0210, Project A-1572

Gentlemen:

During the current report period, the greater part of the experimental program has been completed. Tasks remaining are measuring drying shrinkage for the aggregate cast samples and determining creep rates. These tasks will be completed during the current report period. A draft of the final report is being written and should be completed by the end of this report period.

Respectfully submitted,

Joe N. Harris
Project Director

jw
AGGREGATE CASTING TECHNIQUES FOR PRODUCING HIGH DENSITY SLIP-CAST FUSED SILICA RADOMES

By

E. A. Welsh and J. N. Harris

Contract DA-AH01-74-C-0210

Prepared for
U. S. Army Missile Command
Redstone Arsenal, Alabama 35809

July 1974

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

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AGGREGATE CASTING TECHNIQUES FOR PRODUCING HIGH DENSITY SLIP-CAST FUSED SILICA RADOMES

By
E. A. Welsh and J. N. Harris

Contract DA-AH01-74-C-0210

Prepared for
U. S. Army Missile Command
Redstone Arsenal, Alabama 35809

July 1974

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

Distribution limited to U. S. Government Agencies only; other requests for this document must be referred to U. S. Army Missile Command (AMSMI-RSM).
FOREWORD

This program was conducted by the High Temperature Materials Division, Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia 30332. The work was performed under U. S. Army Contract DA-AH01-74-C-0210. Mr. Phil Ormsby of the Ground Equipment & Materials Directorate, U. S. Army Missile Command was the Technical Director.

The period of performance was 4 October 1973-4 July 1974. Principal personnel contributing to this program were J. N. Harris, E. A. Welsh, M. L. Calhoun, J. D. Walton, Jr. and N. E. Poulos.
ABSTRACT

This program investigated aggregate casting of fused silica as a means of reducing drying and sintering shrinkage in the production of slip-cast fused silica. The efficiency of particle packing was increased so that green bulk densities greater than 2.0 gm/cm$^3$ were achieved. Drying shrinkage was reduced to essentially zero. Sintered properties dependent on bulk density such as dynamic elastic modulus and dielectric constant had the same values as slip-cast fused silica of the same density. Transverse strength which is dependent on the degree of sintering ranged from 25 to 60 percent as strong as slip-cast fused silica of 1.95 gm/cm$^3$ density. Transverse strength decreased as aggregate particle size increased. Methods for increasing this strength would be to obtain a more active aggregate by eliminating surface impurities or to decrease the mean particle size of the starting materials both slip and aggregate. Surface grinding was limited to machining of dielectric specimens, but no problems were encountered with grain pull out.
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I. OBJECTIVE

The objective of this program is to investigate aggregate casting as a means of reducing drying and sintering losses in the production of slip-cast fused silica radomes.

II. INTRODUCTION

One of the most critical areas in the slip casting of fused silica radomes is the drying process. Conventional, as cast, fused silica has a porosity of about 17 volume percent. At the end of casting, the pore spaces in the cast part are filled with water and a thin film of water surrounds each particle. Since the particles are not in direct contact but are cushioned by a thin water layer, the cast part has very little strength and will slump slightly if removed from the mold. At this point, casting from slips with 7-8 micrometer (μm) mean particle diameters will contain approximately 8.5 to 10 percent water, depending on the packing efficiency of the particle size distribution.

As drying progresses water is removed from the system bringing the particles closer together until finally at the "critical moisture content," the particles are in contact. Numerous studies have indicated that the bulk of the drying shrinkage occurs during this period. Measured values for drying shrinkage of castings from 7-8 μm mean particle diameter silica slips indicate drying shrinkages in the range from 0.05 to 0.1 percent. Since these measurements were referenced to model size rather than actual mold size, the linear drying shrinkage is more probably in the range from 0.2 to 0.4 percent allowing for plaster mold setting expansion of approximately 0.2 percent. This shrinkage corresponds to a small moisture reduction on the order of 0.5 to 0.7 percent. At this point and certainly by the time 1.0 percent moisture has been removed from the cast part, the part may be safely removed from the mold.
Thus, the two most important points in drying large slip-cast fused silica shapes are:

(1) Drying should be carried out in the mold until the moisture content drops below the critical point (from 0.5 to 1 percent loss).

(2) Drying rate during this time should be slow enough that moisture gradients across the cast wall are not large enough to cause cracking from differential shrinkage. These conditions are difficult to estimate or define from existing data and must be determined by trial and error for the particular part and mold configuration used. (Drying rate is also restricted by mean particle diameter. Finely ground slips form cast parts with smaller and, therefore, less permeable pores.)

After the critical moisture content is reached, the part may be rapidly dried. Small shapes have been successfully dried at 350° F, but for most shapes it is recommended that drying temperatures be kept below 125° F. After the moisture content has been reduced to 1 or 2 percent, the part should be dried to at least 250° and preferably 350° F before sintering.

Recent experience at both Georgia Tech and at a radome manufacturer's plant has indicated that more radomes fail in the drying stage of the process than at any other point. In addition, drying schedules of from three to four weeks require a high investment in drying capacity and mold handling equipment. Any improvement in the drying process would result in greater production capacity and a much lower reject rate on radome blanks.
A study paralleling work at Georgia Tech on slip casting of fused silica has been conducted in the USSR since approximately 1967. The major difference in the Russian work and the work conducted in the U. S. is in the purity of the fused silica slips. The Russians start with a high purity silica glass of the quality of the General Electric or Sylvania material used in studies at Georgia Tech. However, to keep contamination to the barest minimum they grind the glass in fused quartz mills using fused quartz media. Their initial work followed the same casting method as used in the U. S. That is, they wet ball milled the glass to a slip and cast in conventional plaster molds 1/. Since this initial work their casting procedures have evolved into an "aggregate" casting technique 2/, where particles up to ten times the maximum particle diameter in the slip are added. By this technique green bulk densities of 1.92 to 2.03 gm/cc have been reported by the Russians 3/. Typical green bulk densities for castings using conventional U. S. slips are 1.81 gm/cm$^3$ 4/ to 1.85 gm/cm$^3$ 5/.

A limited amount of aggregate casting work was accomplished at Georgia Tech in the late 50's and early 60's, where large thick sections were required. However, these castings contained particles as large as 600 μm and no efforts were made to optimize particle packing. Therefore, the densities of these castings were of the same order as the conventional slip-cast fused silica.

Drying would be improved in two ways by aggregate casting. First and most important, the number of particle to particle contacts per unit volume would be reduced substantially, which in turn will reduce the drying shrinkage, and increase the rate at which the part can be dried without failure due to stresses resulting from moisture/shrinkage gradients across the radome wall. Second, the total volume of water to be removed will be reduced, shortening drying times even further. Finally, with a higher cast density, sintering time and shrinkage can be reduced, resulting in further cost savings.
The highest attainable cast density may not be practical for slip-cast fused silica radomes due to the possibility of more severe rain erosion damage with a denser structure. Also, the tensile strength with respect to density is dependent on time-temperature of sintering. Therefore, it may be necessary to limit the cast density to ensure that sufficient sintering is attained to reach maximum strength.
III. EXPERIMENTAL PROGRAM

A. Literature Survey

A brief review of prior work in the area of powder packing was carried out to ensure a reasonable basis for selection of initial composites. One of the earlier and perhaps the simplest treatments of packing of binary mixtures was a study by Westman and Hugill 6/. Packing efficiency of a binary powder mixture is described in terms of a parameter $V_a$, which is referred to as an apparent volume and is defined by the relationship

$$ V_a = \frac{1}{1-f_v} = \frac{\rho_T}{\rho_B} $$

(1)

where $f_v$ = void fraction in packing

$\rho_T$ = theoretical density

$\rho_B$ = bulk density

The limiting densities (in terms of $V_a$) for mixtures of two powders can be determined graphically, as in Figure 1. The horizontal line at $V_a = 1.00$ represents the true volume of the powder mixture, i.e., for two powders of the same specific gravity, the theoretical density of the material. The points C and F represent the appropriate apparent volumes for the coarse and fine components. In this case the porosities of the coarse and fine components are taken as 40 percent and 18 percent respectively (approximate values for sized fused silica grain and slip) 7,8/.

Assuming that the coarse powder is several orders of magnitude greater in diameter than the fine powder, the following arguments can be made. As fine powder is added to coarse powder, it initially fills in the voids between the coarse particles without increasing the total
Figure 1. Packing Diagram for Mixtures of Slip and Grain
volume of the system. This situation is represented by a straight line connecting point C with the lower right hand portion of the diagram. The relationship breaks down at the point where the fine particles just fill the void spaces in the coarse packing, but the initial trend is along the line described.

On the other hand, adding coarse particles to a packing of fine particles tends to reduce the void volume. Also, since the coarse particles are theoretically dense and are immersed in a second phase (the fine packing which has porosity) the effect is to drive the void volume along the straight line connecting point F with the point $V_a = 1.00$ on the left hand side of the diagram. This relationship breaks down at the point when the coarse particles have been added in sufficient quantity to touch each other. The intersection of the two lines is the point of maximum density for the system, i.e., the point where the voids in the coarse packing are completely filled with the fine component. The straight lines connecting this intersection with points C and F represent the limiting void volumes for the system and represent the situation where the ratio of the coarse and fine particles approaches infinity. The other limiting case, where the diameters of the coarse and fine powders are equal is simply the straight line connecting points C and F. A real packing will usually fall short of the lower limits by a value dependent on the ratio of the coarse and fine component diameter.

A more useful type of approach would be a method which describes bulk density directly instead of having to transform the parameter $V_a$ into bulk density. This has been done by Rose and Robinson 9/. They introduce the concept of a critical mass ratio, i.e., the mass fraction of the coarse component at the point where the coarse particles just touch, and the interstices are completely filled with the finer component. The ratio may be estimated from
\[ F_c = \frac{1}{\delta_2 \left( \frac{\rho_2}{\delta_1} \frac{\delta_1}{\rho_1} \right) + 1} \]  

(2)

where \( \rho_1 \) and \( \rho_2 \) are the specific gravities of the coarse and fine components, and where \( \delta_1 \) and \( \delta_2 \) are the normal bulk densities of the coarse and fine components.

For a mass ratio less than critical, the situation where coarse grains are being added to the fine component they derive the relationship

\[ \delta = \frac{\delta_1 \delta_2}{F \left[ \frac{1-F}{F} - \left( \frac{1-F}{F_c} \right) \right] + \delta_2} \]  

(3)

where \( F = \) mass fraction coarse component

\( F_c = \) critical mass ratio

\( \delta_1 = \) bulk density of coarse component

\( \delta_2 = \) bulk density of fine component

For the case where the mass ratio is greater than critical, the case where the fine component is being added to the coarse packing, the bulk density of the mixture is given by

\[ \delta = \frac{\delta_1}{F} \]  

(4)

As before, these are limiting values and assume perfect mixing of two components with an infinite size ratio. A lower limit can also be defined for the case where the particle diameters are the same, or
where there is complete segregation of the two components. Under these circumstances, the bulk density of the mixture is given by

\[ \delta = \frac{\delta_1 \delta_2}{F(\delta_2 - \delta_1) + \delta_1} \]  \hspace{1cm} (5)

where the variables are as previously defined. These upper and lower limiting densities are shown in Figure 2. Although a rigorous numerical comparison has not been made, these results are virtually identical with results from transforming the values of Westman and Hugill 6/ to bulk density.

In actuality, the upper limiting densities are approached but not reached. The previously mentioned authors have explained this in terms of the ratio of the component diameters and the degree of mixing. Karlsson and Spring 10/ present a third view. They suggest that there is a volume expansion on mixing, such as when a small particle comes to rest between two large particles rather than in the void between them. They empirically derive a series of correction factors based on the radius ratio of the components and the mass fraction of each. The experimental effort required to measure the proper factors for each system studied appears to outweigh the benefit of better prediction.

The above mentioned studies are all of value in predicting bulk densities for silica slip-aggregate mixtures. However, some data on aggregate casting of fused silica is available in the Russian literature. References 2/ and 3/ deal primarily with the theory and mechanism for obtaining high density castings, while references 11,12,13/ deal with the problems of keeping the aggregate in suspension for satisfactory casting. Pivinskii 2/ states that for a granular filler saturated by a much finer bonding phase (fused silica slip), the packing efficiency of the aggregate cast body is given by
Figure 2. Bulk Density versus Weight Percent Fine Component for Aggregate Cast Fused Silica
\[ K_p = K_B + K_g (1 - K_B) \]  

(6)

where \( K_B \) = packing efficiency of bonding phase (fines)

\( K_g \) = packing efficiency of filler

For the case of a fused silica slip with a packing efficiency of 82 percent and a coarse aggregate of 65 percent packing efficiency, the maximum packing is estimated at approximately 94 percent. He further suggests that the minimum grain size in the aggregate be at least an order of magnitude greater than the maximum particle size in the slip. In a mixture containing 40 percent slip and 60 percent aggregate ranging from 1.0 to 1.2 mm in diameter, the reported bulk density of the casting is from 95.5 to 96 percent of theoretical density.

In reference 3/, Pivinskii again reports that; provided the coarse aggregate can be held in suspension, the bulk density of the castings can be predicted from the expression

\[ \rho_c = V_g \rho_T + (1 - V_g) \rho_o \]  

(7)

where \( V_g \) is the volume fraction granular filler given by

\[ V_g = \frac{W_g}{(\rho_T/\rho_o)} \]  

(8)

and where \( W_g \) = weight fraction granular filler

\( \rho_T \) = specific gravity of solid phase

\( \rho_o \) = bulk density of castings from unmodified slip

This is a much simpler version of Equation (3). He points out that the relationship breaks down for castings with greater than 60-65 percent aggregate since at that point there is insufficient slip to fill the voids in the aggregate network and large pores develop. It is also
reported that the casting rate of the aggregate filled materials is much faster than that of normal slip. This agrees with the concept that casting rate is a function of the permeability of the cast wall, which in turn varies inversely with the surface area of the cast wall. The addition of a coarse aggregate to a slip lowers the specific surface drastically.

B. Technical Grade Aggregate Systems

To begin studies of the behavior of aggregate loaded casting slips, technical grade materials were investigated. These were readily available at low cost and provided materials for study until high purity material could be obtained.

Fifteen gallons of technical grade slip particle size range (44 µm to sub µm) and 100 pounds each of -10 +20 mesh particle size range (200° to 840 µm) and -20 +50 particle size range (297 to 840 µm) mesh technical grade fused silica were obtained from Glasrock Products, Inc., Calhoun, Georgia.

Particle size analyses for the granular materials were made by screen analysis, while particle size distribution for the slip was performed according to ASTM standard test method D422, a hydrometer method. Results of the three analyses are plotted in Figure 3. From this figure it can be seen that the two grain distributions are slightly overlapping and provide a continuous range of particles over nearly two orders of magnitude.

Microscopic examination of the grain indicated a fine closed pore structure. Pycnometer determinations of the density of various size fractions are shown in Figure 4. The density of the +10 mesh fraction was in the same range as slip-cast hardware. The fraction from 10 to 20 mesh fell on a straight line when plotted on a semi-logarithmic paper. From extrapolation the liberation size of the pores (i.e., the
Figure 3. Particle Size Distributions of Technical Grade Aggregate and Slip
Figure 4. Bulk Density versus Particle Diameter for Technical Grade Fused Silica Grain
size at which no particle contains a closed pore) is estimated at approximately 300 microns or 50 mesh. This means that the use of very large aggregate grains may prevent obtaining maximum density. However, a slip-cast material should contain no closed pores within the grains themselves.

A series of 3/4 x 3/4 x 6 inch test bars were cast from several compositions. The mold consisted of a polycarbonate frame fitted with 3/4 x 1/8 x 10 inch polycarbonate dividers. The individual mold cavities formed by the spaces between the divider were closed on one side by a flat polycarbonate plate, and on the other side with a plaster slab. The casting slip was poured from one end. In this way samples were cast in only one direction rather than radially as in the case for cylindrical mold cavities. After casting was completed the plaster plate was removed and the bars dried in the mold for 3 to 4 hours at 125o F. At this point the divider strips were removed, leaving the bars which were then removed from the cover plate and dried at 350o F prior to sintering.

The compositions examined were the following ratios of grain to slip: 65/35, 60/40, 55/45, 50/50, 45/55. Both -10 +20 and -20 +50 mesh grain were used. Bars could not be cast successfully from the two extreme compositions. The 65/35 mixture did not contain enough slip to fill the interstices between the aggregate grains. When sufficient water was added to make the mixture pourable, the slip would accumulate in the lower portions of the casting, leaving a mass of slip coated grains at the top of the casting. This portion of the casting crumbled easily and could not be handled. At the other extreme, the 45/55 mixture had an excess of slip and the aggregate grains tended to settle in the lower portions of the sample leaving a layer of essentially slip-cast material in the upper portion of the samples. The other mixtures were successfully cast although small additions of water were necessary with the -20 +50 mesh grain and mild
vibration of the mold was helpful in reducing voids. It was also beneficial to pre-wet the mold, since the casting rate of the aggregate cast samples is much higher than for a slip-cast body.

The dried samples were bisque fired for one hour at 1500 °F. This was sufficient to bond the samples enough to carry out porosity and bulk density measurements using water immersion.

The bulk densities after bisque firing for the technical grade samples are shown in Figure 5. As with Figure 2, the solid line represents the theoretical limit on bulk density. From left to right, the vertical clusters of samples represent compositions with grain/slip ratios of 60/40, 55/45 and 50/50. The data points are shifted toward the grain side of the diagram due to correction for the water content of the slip. The open circles represent -20 +50 mesh samples, while the other samples are made with -10 +20 mesh grain.

Samples from each group were fired for 2 and 3 hours at 2200 °F. Bulk density, porosity, specific gravity, dynamic Young's modulus, and modulus of rupture were measured for each sample. With the exception of the slip-cast fused silica controls, the 2 and 3 hour samples were statistically indistinguishable. Table I lists averaged values of bisque fired bulk density, sintered bulk density, percent change in bulk density (directly related to sintering shrinkage), sintered dynamic Young's modulus, and modulus of rupture for each composition. It should be noted that the set of bars containing 50 percent grain was inadvertently sintered 3 hours at 2300 °F, resulting in a percent change in bulk density approaching that obtained with the slip-cast fused silica controls. At this point, devitrification effects can be seen in the form of reduced modulus of rupture in comparison with shrinkage. However, the ratio of modulus of rupture to dynamic Young's modulus, an estimate of the failure strain is nearly the same as for the other samples. As will be discussed later,
Figure 5. Bulk Density versus Composition for Technical Grade Aggregate Cast Fused Silica
## TABLE I

**PHYSICAL AND MECHANICAL PROPERTIES OF TECHNICAL GRADE AGGREGATE CAST FUSED SILICA**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percent Size</th>
<th>Cast Bulk Density (gm/cm³)</th>
<th>Sintered Bulk Density (gm/cm³)</th>
<th>Percent Densification (%)</th>
<th>Sintered Dynamic Young's Modulus (psi)</th>
<th>Sintered Modulus of Rupture (psi)</th>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 -10 +20</td>
<td>1.87 ± 0.03</td>
<td>1.89 ± 0.03</td>
<td>0.92 ± 0.18</td>
<td>3.9 ± 0.4 x 10⁶</td>
<td>640 ± 290</td>
<td></td>
</tr>
<tr>
<td>55 -10 +20</td>
<td>1.90 ± 0.04</td>
<td>1.92 ± 0.03</td>
<td>0.99 ± 0.39</td>
<td>4.1 ± 0.6 x 10⁶</td>
<td>1200 ± 200</td>
<td></td>
</tr>
<tr>
<td>50 -10 +20</td>
<td>1.96 ± 0.01</td>
<td>2.03 ± 0.01**</td>
<td>3.87 ± 0.18**</td>
<td>5.7 ± 0.1 x 10⁶**</td>
<td>1450 ± 130**</td>
<td></td>
</tr>
<tr>
<td>55 -20 +50</td>
<td>1.82 ± 0.01</td>
<td>1.84 ± 0.01</td>
<td>1.47 ± 0.12</td>
<td>3.3 ± 0.1 x 10⁶</td>
<td>820 ± 90</td>
<td></td>
</tr>
<tr>
<td>100 - Slip</td>
<td>1.8 ± 0.01</td>
<td>1.91 ± 0.01</td>
<td>4.00 ± 0.29</td>
<td>4.2 ± 0.2 x 10⁶</td>
<td>3826 ± 370</td>
<td></td>
</tr>
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</table>

*Except as indicated, data is averaged over sintering times of both 2 and 3 hours at 2200°F.*

**Bars sintered 3 hours at 2300°F.**
this suggests that the possible strength reduction due to the presence of large grains in the structure far outweighs the strength reduction due to devitrification. A duplicate set of bars for sintering at 2200°F was prepared, but was not sintered since it was felt that effort would be better spent in developing high purity materials.

To gain further insight on the sintering characteristics and the factors affecting strength of aggregate cast materials, a multiple linear regression analysis was performed on the data from the sintering studies. The dependent variable, modulus of rupture, was evaluated in terms of the independent variables volume fraction grain, and sintering time. For analysis purposes, dry bulk density, sintered bulk density, sintered Young's modulus, and percent change in bulk density during sintering were included as independent variables, when in reality, they are dependent on composition and sintering time. The correlation coefficient matrix for the analysis is shown in Table II, and represents the linear correlation coefficients for all combinations of variables. A high correlation coefficient for a combination of two dependent variables is not always indicative of a strong correlation as is shown in Figure 6 for the case of modulus of rupture and percent sintering densification. In this case the data is clustered around two widely separated points, with each cluster by itself having low correlation but having a high correlation in combination. On the other hand, high correlations between an independent and a dependent variable are generally quite reliable as shown in Figure 7 which illustrates the effect of the composition on modulus of rupture. In view of this, the following points should be made:

(1) Modulus of rupture is lowered by increasing the grain content of the composition.

(2) Sintering time has little or no effect on the strength of the material, at least for the conditions examined.
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<th>Sintering Time</th>
<th>Sintered Bulk Density</th>
<th>Sintered Young's Modulus</th>
<th>Percent Change in Bulk Density</th>
<th>Modulus of Rupture</th>
</tr>
</thead>
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<tr>
<td>Volume Fraction</td>
<td>0.7013</td>
<td>0.0727</td>
<td>-0.0278</td>
<td>-0.1492</td>
<td>-0.9779</td>
<td>-0.9648</td>
</tr>
<tr>
<td>Grain (&lt;0.001)</td>
<td>(NC)</td>
<td>(&lt;0.001)</td>
<td>(NC)</td>
<td>(NC)</td>
<td>(&lt;0.001)</td>
<td>(&lt;0.001)</td>
</tr>
<tr>
<td>Dry Bulk Density</td>
<td>---</td>
<td>0.1608</td>
<td>0.6797</td>
<td>0.4341</td>
<td>-0.6462</td>
<td>-0.6047</td>
</tr>
<tr>
<td></td>
<td>(NC)</td>
<td>(&lt;0.001)</td>
<td>(&lt;0.05)</td>
<td>(&lt;0.001)</td>
<td>(&lt;0.001)</td>
<td>(&lt;0.005)</td>
</tr>
<tr>
<td>Sintering Time</td>
<td>---</td>
<td>---</td>
<td>0.2594</td>
<td>0.4423</td>
<td>0.0530</td>
<td>0.0132</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(NC)</td>
<td>(&lt;0.05)</td>
<td>(NC)</td>
<td>(NC)</td>
</tr>
<tr>
<td>Sintered Bulk Density</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.8017</td>
<td>0.1205</td>
<td>0.1538</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(&lt;0.001)</td>
<td>(NC)</td>
<td>(NC)</td>
</tr>
<tr>
<td>Sintered Young's Modulus</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.2473</td>
<td>0.2734</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(NC)</td>
<td>(NC)</td>
</tr>
<tr>
<td>Percent Change in Bulk Density</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.9787</td>
<td>(&lt;0.001)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: 1. Figures in parenthesis indicate probability of obtaining same degree of correlation from a sample of the same size drawn from a random population.

2. NC indicates non-significant correlation.
Figure 6. Modulus of Rupture versus Percent Sintering Densification for Technical Grade Aggregate Cast Fused Silica and Slip-Cast Fused Silica
Figure 7. Modulus of Rupture versus Weight Percent Fine Component for Aggregate Cast Fused Silica
(3) Modulus of rupture is somewhat dependent on sintering shrinkage, but totally independent of sintered bulk density.

(4) Young's modulus seems to be related more directly to sintered density.

The first three points are in agreement with conclusions reached on an earlier program where silicon carbide powders were added to silica slip 14/. In that program the data suggested that the additive powders were not participating in sintering and were behaving as voids in the sintered product. The current data lead to the same conclusion. Frenkel 15/ has developed an expression for sintering of glass powders in which the shrinkage at any time t, is given by

\[
\frac{L}{L_o} = 1 - \frac{\gamma t}{2\eta a}
\]  

(9)

where \( L \) = linear dimension at time \( t \)

\( L_o \) = the initial linear dimension

\( \gamma \) = the surface tension

\( \eta \) = the viscosity

\( a \) = the average particle radius

This relationship suggests that the aggregate grains simply do not have sufficient surface energy to sinter.

At this point work was halted on technical grade materials and efforts with high purity materials were begun. Proprietary work under an industrial sponsor had suggested that high purity materials were much more highly reactive than technical grade silicas and it was felt that higher strength materials could be developed.
C. High Purity Aggregate Systems

Fused silica tubing cullet was used as a source of high purity aggregate. A major problem in grinding relatively coarse aggregate in a ball mill is in keeping the product from being overground. Grinding times for each batch must be comparatively short. Since personnel were not available to use a 50 gallon ball mill at a local fused silica products manufacturer's plant, a decision was made to grind the material in house using small, one gallon mills. In order to estimate the production rate and efficiency of this type operation a brief grinding study was carried out.

A one gallon 85 percent alumina jar mill was loaded with 1000 gms fused silica cullet and either 1000 or 2000 gms 85 percent alumina grinding media. The mill was operated for a fixed amount of time and the contents screened. The undersize and product were saved, while the oversize and fresh feed in the same amount as the product and undersize removed was added. The cycle was repeated until the weight of the product and undersize per cycle reached a constant value. A production rate based on a cycle time of 15 minutes plus the grinding time, and a percent recovery based on the ratio of product to undersize were calculated as shown in Table III. The product in all cases was -10 +20 grain, the coarsest grain used in the program.

Method 1 was followed for the production of aggregate. Lower grinding times were not investigated since the results showed a rapid drop in percent recovery with increasing time.

A total of 4 Kg -10 +20 grain, 2.5 Kg -20 +50 inch grain, and 1.5 Kg -50 mesh grain were produced by this method. The grains were cleaned by soaking overnight in a solution of aqua regia diluted 3:1 with water. The grain was then washed to remove the excess acid and impurities. Particle size distributions for the three grain fractions and for the high purity slip used in the program are shown in Figure 8.
Figure 8. Particle Size Distributions of High Purity Aggregate and Slip
TABLE III
PRODUCTION DATA FOR -10 +20 MESH
HIGH PURITY FUSED SILICA GRAIN

<table>
<thead>
<tr>
<th>Method</th>
<th>Method 1</th>
<th>Method 2</th>
<th>Method 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of Grinding Media</td>
<td>2000 gms</td>
<td>2000 gms</td>
<td>1000 gms</td>
</tr>
<tr>
<td>Grinding Time</td>
<td>10 min</td>
<td>5 min</td>
<td>10 min</td>
</tr>
<tr>
<td>Production Rate*</td>
<td>233 gm/hr</td>
<td>219 gm/hr</td>
<td>125 gm/hr</td>
</tr>
<tr>
<td>Percent Recovery</td>
<td>40.4%</td>
<td>47.7%</td>
<td>51-5</td>
</tr>
</tbody>
</table>

*Based on Cycle Time of 15 min. + Grinding Time.

The three grain size distributions along with the slip gave a continuous range of particle sizes over four orders of magnitude. A pycnometer density check on both coarse grain and slip gave specific gravities in the range 2.22 gm/cm³, the theoretical density of the material.

To further characterize the particles and slip, the surface area of each size fraction was determined using the BET gas adsorption technique by Micromeritics Instrument Corporation, Norcross, Georgia. Values for surface area along with mean particle diameter, tapped bulk density and packing efficiency are shown in Table IV.

Packing efficiency for monofraction grains usually decreases with decreasing grain size. The -50 mesh grain and slip have higher than expected packing efficiencies since the distribution are noticeably broader, as shown by the lower slope of the size distribution curves.

In an effort to obtain better values for packing efficiency of the various possible compositions a series of samples were cast and subjected to mercury intrusion porosimetry. From these experiments the following data were obtained: pore size distribution, bulk density,
TABLE IV
SURFACE AREA AND PACKING EFFICIENCY FOR HIGH PURITY AGGREGATE AND SLIP

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Surface Area</th>
<th>Bulk Density</th>
<th>Packing Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean Diameter</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(micrometers)</td>
<td>(m²/gm)</td>
<td>(gm/cm³)</td>
</tr>
<tr>
<td>-10 +20</td>
<td>1400</td>
<td>0.0126</td>
<td>1.230</td>
</tr>
<tr>
<td>-20 +50</td>
<td>550</td>
<td>0.0230</td>
<td>1.216</td>
</tr>
<tr>
<td>-50</td>
<td>110</td>
<td>0.85</td>
<td>1.294</td>
</tr>
<tr>
<td>Slip</td>
<td>7.5</td>
<td>4.597</td>
<td>1.84 (est)</td>
</tr>
</tbody>
</table>

specific gravity, and percent porosity. Compositions studied were 45, 50, 55 and 60 percent by weight grain for grain sizes of -10 +20 mesh, -20 +50 mesh and -50 mesh. Results are shown in Table V.

This data must be viewed with some suspicion since the specific gravity of the material is known to be approximately 2.22 grams/cm³. The data are most suspect in the case of fused silica slip. The most probable cause of these errors lies in the fact that the bulk volume of the sample is measured indirectly by weighing the amount of mercury necessary to fill the volume between the sample and the sample cell wall. Errors here can be compounded in the subsequent calculations. The data are presented graphically in Figure 9. The scatter in the data may be due to normal sample variation, but the data again illustrate a point made during the previous investigation on the effect of powder additives to silica slip, namely, that the density of the casting is lowered by using finer particle size fillers.

Since only limited amounts of high purity aggregate were available, a method described by Cutler [16] was used to determine sintering rates over a wide range of temperatures. The shrinkage
Figure 9. Bulk Density versus Composition for High Purity Aggregate Castings
TABLE V
RESULTS OF MERCURY INTRUSION POROSIMETRY ON HIGH PURITY AGGREGATE CAST SAMPLES

<table>
<thead>
<tr>
<th>Composition</th>
<th>Weight Percent Grain Size (mesh)</th>
<th>Average Pore Diameter (micrometers)</th>
<th>Hg Density @ 50,000 psi</th>
<th>Bulk Density (gm/cm³)</th>
<th>Specific Gravity (gm/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 10/20</td>
<td>0.072</td>
<td>1.93</td>
<td>2.07</td>
<td>6.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 10/20</td>
<td>0.086</td>
<td>1.95</td>
<td>2.09</td>
<td>6.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55 10/20</td>
<td>0.066</td>
<td>1.94</td>
<td>2.08</td>
<td>6.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 10/20</td>
<td>0.18</td>
<td>1.95</td>
<td>2.14</td>
<td>8.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45 20/50</td>
<td>0.082</td>
<td>1.88</td>
<td>2.06</td>
<td>8.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55 20/50</td>
<td>0.14</td>
<td>1.89</td>
<td>2.13</td>
<td>11.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 20/50</td>
<td>0.29</td>
<td>1.90</td>
<td>2.22</td>
<td>14.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45 -50</td>
<td>0.52</td>
<td>1.75</td>
<td>2.13</td>
<td>17.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 -50</td>
<td>0.43</td>
<td>1.72</td>
<td>2.18</td>
<td>20.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55 -50</td>
<td>0.65</td>
<td>1.71</td>
<td>2.17</td>
<td>21.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slip</td>
<td>0.06</td>
<td>1.59</td>
<td>1.80</td>
<td>11.57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Sample with 60% -50 grain too fragile to handle. Sample with 50% -20 +50 grain broken in handling.

The rate for a compact of spherical glass particles may be described by the following equation, which is a form of Equation 9.

\[
\frac{d \left( \frac{\Delta L}{L_0} \right)}{dt} = \frac{\gamma}{2a L_0^n} \quad (10)
\]

where \( \frac{\Delta L}{L_0} \) = fractional shrinkage in some linear dimension
\( t \) = time
\[ \gamma = \text{surface tension} \]
\[ a = \text{particle radius} \]
\[ \eta = \text{viscosity} \]

The viscosity, \( \eta \), can be approximated over a small range of temperature by

\[ \eta = A \exp \left( \frac{Q}{RT} \right) \] (11)

where \( A = \text{pre-exponential viscosity term} \)
\( Q = \text{activation energy} \)
\( R = \text{gas constant} \)
\( T = \text{absolute temperature} \).

This relationship is valid only over a limited range of temperature since \( Q \) and \( A \) both vary slightly with temperature.

If the sample is heated at a constant heating rate, such that the temperature is given by

\[ T = ct \] (12)

where \( c = \text{heating rate} \)

Writing Equation 10 in terms of Equations 11 and 12 gives

\[ \frac{d}{dt} \left( \frac{\Delta L}{L_0} \right) = \frac{\gamma}{2acA} \exp \left( -\frac{Q}{RT} \right) \] (13)

which indicates that a plot of \( \ln \left( \frac{d}{dt} \left( \frac{\Delta L}{L_0} \right) \right) \) versus \( 1/T \) should be linear with a slope of \( -Q/R \). This, of course, requires that the
surface tension and the pre-exponential term remain constant, which is not unreasonable.

By sintering samples in an automatic recording dilatometer, plots of \( \frac{d}{dt} \left( \frac{\Delta L}{L_0} \right) \) versus (1000/T) can be made and sintering rates as well as activation energies can be calculated directly. The sintering rates are in terms of rate of change of temperature, but can be converted to a time basis by multiplying by the rate of temperature increase \( c \).

Samples of high purity slip-cast fused silica, and high purity aggregate cast fused silica were prepared. The aggregate cast samples were equal parts by weight of slip and the three aggregates -10 +20 mesh, -20 +50 mesh, and -50 mesh, for a total of four samples. Samples were cast in Teflon<sup>®</sup> cylinders 3/8 inch inside diameter by 1.3 inches long. The cylinder was placed on a plaster slab and filled to slightly below the top with the mix. After the casting had been formed it was capped by casting a layer of slip over the exposed end of the sample. After drying the excess slip was ground off flush with the top of the Teflon<sup>®</sup> mold, leaving a cylindrical sample with smooth parallel ends. The samples were pressed from the mold with a brass rod and hydraulic press. The samples were sintered to 1450° C at a heating rate of approximately 200° C per hour. The dilatometer controller increased the temperature by driving the set point up at a constant rate. Since the thermocouple response was not completely linear the resulting heating curve departs slightly from linear as shown in Figure 10. Curves for total shrinkage versus temperature are shown in Figure 11. The two coarser grain samples sintered at identical rates up to approximately 1375° C, at which point the rate for the -10 +20 mesh material dropped off considerably. Plots of \( \ln \frac{d}{dt} \left( \frac{\Delta L}{L_0} \right) \) versus 1000/T are shown in Figure 12. Again data for the two coarser aggregates overlapped and only a single curve is shown.
Figure 10. Temperature versus Time for Automatic Recording Dilatometer at Nominal Heating Rate of 200°C Per Hour
Figure 11. Fractional Shrinkage versus Temperature for High Purity Slip and Aggregate Cast Material
Figure 12. Plot of Sintering Function versus Reciprocal Temperature
The data can be explained most readily in terms of the surface area of the compositions. Assuming that the surface areas of each component are additive, the surface areas for the samples are shown in Table VI.

**TABLE VI**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Specific Surface Area ($m^2/gm$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% -10 +20 mesh grain</td>
<td>2.098</td>
</tr>
<tr>
<td>50% -20 +50 mesh grain</td>
<td>2.104</td>
</tr>
<tr>
<td>50% -50 mesh grain</td>
<td>2.555</td>
</tr>
<tr>
<td>100% slip</td>
<td>4.957</td>
</tr>
</tbody>
</table>

Sintering rates are then seen to be proportional to surface area, which for the case of the two coarsest grain fractions are practically identical. Another point is that the slopes of the $d(\Delta L/L_0)/dt$ lines for all compositions are almost the same. Calculated values for activation energy range from 70 to 80 kcal/gm, approximately one-half the usual value for viscosity 17/. Cutler 16/ explains this in terms of a tendency for irregular or elongate particles to lower their surface energy by becoming more rounded, an action that appears as an increase in the sintering rate or a lowering of the activation energy. The data also indicated that higher than normal sintering temperatures might be useful. Previous work at Georgia Tech 8/ indicated that high purity slip-cast fused silica could be sintered at temperatures as high as 2500° F without excessive devitrification. Therefore, the next sintering studies were made at 2300° and 2400° F.
To verify the constant heating rate data and to provide mechanical property data, a series of 3/4 x 3/4 x 6-inch bars were cast from the 50/50 mixtures of the three grain sizes with slip. To conserve grain single samples were sintered at 2300°F for times ranging from one to six hours in one hour increments, and at 2400°F for one and two hours. A single bar was fired three hours at 2400°F but its sintered density was lower than the other bars in the series, indicating excessive microcracking of the structure through devitrification.

Although more densification took place and although a wider range of sintering times were investigated, some useful conclusions can be reached by averaging data for all compositions as in the data shown in Table VII. The grouping of data from a wide range of sintering times exaggerates confidence intervals and in the case of modulus of rupture lead to values that are not significantly different statistically. Nevertheless, several trends can be seen. As with the technical grade aggregate castings, the cast and sintered bulk densities decrease with decreasing aggregate grain size while sintering rates increase. Another similarity is that the dynamic modulus is strictly a function of density and appears to have no relationship at all to the amount of sintering shrinkage. Inspection of the raw data shows that all three compositions have maximum flexural strengths in the range 2000 to 2600 psi and that as expected the high purity aggregates in general have higher flexural strengths than the technical grade materials, indicating greater reactivity during sintering.

Bulk density versus sintering time and temperature for the high purity aggregate cast samples is shown in Figure 13. The high purity material was more reactive than the technical grade material, but still not as reactive as high purity slip-cast fused silica apparently due to the much lower surface area. As before, the -50 mesh grain composition had a lower cast bulk density than the other compositions.
### TABLE VII

**PHYSICAL AND MECHANICAL PROPERTIES OF HIGH PURITY AGGREGATE CAST FUSED SILICA FROM SINTERING STUDIES**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Cast Bulk Density (gm/cm³)</th>
<th>Sintered Bulk Density (gm/cm³)</th>
<th>Percent Densification</th>
<th>Sintered Dynamic Young's Modulus of Rupture (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 -10 +20</td>
<td>2.001 ± 0.004</td>
<td>2.05 ± 0.02</td>
<td>2.3 ± 1.3</td>
<td>6.3 ± 0.9 x 10⁶</td>
</tr>
<tr>
<td>50 -20 +50</td>
<td>1.889 ± 0.004</td>
<td>1.93 ± 0.02</td>
<td>2.4 ± 1.2</td>
<td>5.4 ± 0.7 x 10⁶</td>
</tr>
<tr>
<td>50 -50</td>
<td>1.752 ± 0.002</td>
<td>1.88 ± 0.03</td>
<td>4.6 ± 1.5</td>
<td>4.0 ± 0.6 x 10⁶</td>
</tr>
</tbody>
</table>

Note: Confidence interval at 95% on Student T Distribution.

Bulk density after one hour at 1500°F.
Figure 13. Bulk Density versus Sintering Time for High Purity Aggregate Cast Fused Silica (50 Percent Slip-50 Percent Grain)
but sintered more rapidly. Sintering rates are shown in Figure 14 which illustrates plots of percent sintering densification versus time. As with the constant rate heating experiments the two coarser grain fractions sinter at approximately the same rate, the main difference being that the -20 +50 mesh grain sinters slightly more in the final stages of sintering. From Figures 13 and 14 it can be seen that sintering has nearly reached an end point after six hours at 2300° F or after two hours at 2400° F.

As before with the technical grade aggregate cast samples, a multiple linear correlation analysis was performed to test for trends in the data as well as for subtle correlations. The surface area of the grain (proportional to the surface area of the sample), the sintering time and sintering temperature were the independent variables while modulus of rupture was used as the main dependent variable. The dependent variables bisque fired bulk density, sintered bulk density, percent densification on sintering, and dynamic Young's modulus were considered as independent variables for the purpose of analysis. The matrix of correlation coefficients is shown in Table VIII.

The only variable other than Young's modulus to have any significant correlation with modulus of rupture is the percent densification on shrinkage, as shown in Figure 15. When values for slip-cast fused silica, a different type of material entirely, are dropped from the analysis it can be seen that there is no correlation between aggregate specific surface area and modulus of rupture. This is despite good correlations between modulus of rupture and percent densification, and between percent densification and aggregate specific surface which is shown in Figure 16. The remaining mechanical property correlation of interest is the strong correlation between sintered bulk density and dynamic Young's modulus, which says in effect, that elastic properties (at least as measured with sonic
Figure 14. Sintering Rate versus Time for Aggregate Cast High Purity Fused Silica
<table>
<thead>
<tr>
<th></th>
<th>Sintering Time</th>
<th>Sintering Temp.</th>
<th>Bisque Bulk Density</th>
<th>Sintered Bulk Density</th>
<th>Percent Densification</th>
<th>Young's Modulus</th>
<th>Modulus of Rupture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Area</td>
<td>0.2337 (NC)</td>
<td>-0.1212 (NC)</td>
<td>-0.9138 (&lt;0.001)</td>
<td>-0.8349 (&lt;0.001)</td>
<td>0.6158 (~0.01)</td>
<td>-0.7383 (NC)</td>
<td>-0.0634 (NC)</td>
</tr>
<tr>
<td>Sintering Time</td>
<td>---</td>
<td>-0.4783 (NC)</td>
<td>-0.187 (NC)</td>
<td>-0.1515 (NC)</td>
<td>0.1735 (NC)</td>
<td>-0.581 (NC)</td>
<td>0.1332 (NC)</td>
</tr>
<tr>
<td>Sintering Temperature</td>
<td>---</td>
<td>---</td>
<td>0.1262 (NC)</td>
<td>0.3459 (NC)</td>
<td>0.5350 (0.02)</td>
<td>0.4865 (NC)</td>
<td>0.2698 (NC)</td>
</tr>
<tr>
<td>Bisque Bulk Density</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.9530 (&lt;0.001)</td>
<td>-0.5632 (0.02)</td>
<td>0.7996 (NC)</td>
<td>0.1246 (NC)</td>
</tr>
<tr>
<td>Sintered Bulk Density</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>-0.2867 (NC)</td>
<td>0.9119 (NC)</td>
<td>0.2944 (NC)</td>
</tr>
<tr>
<td>Percent Densification</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>-0.0437 (NC)</td>
<td>0.4209 (0.1)</td>
</tr>
<tr>
<td>Young's Modulus</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.5053 (0.02)</td>
</tr>
</tbody>
</table>

Notes: 1. Figures in parenthesis indicate probability of obtaining some degree of correlation from a sample of the same size drawn from a random population.
2. NC indicates non-significant or coincident correlation.
Figure 15. Modulus of Rupture versus Percent Sintering Densification for High Purity Aggregate Cast Fused Silica
Figure 16. Percent Sintering Densification versus Aggregate Specific Area for High Purity Aggregate Cast Fused Silica with 50 Percent Aggregate
resonance techniques) are dependent strictly on the mass per unit volume and are affected to a lesser degree by the degree of bonding between the particles as indicated by flexural strength. These correlations are shown graphically in Figures 17 and 18, respectively. The remaining strong correlation between aggregate specific surface area and cast bulk density reinforces the notion that for narrow size distribution powders, additions of finer grain sizes to slip disrupt the packing and decrease the cast density.

A series of scanning electron micrographs were taken to show the morphology of the fracture surfaces. Figures 19 through 22 show fracture surfaces for the highest strength samples with 50 percent -10 +20, -20 +50, and -50 mesh grain, and a slip-cast fused silica control sample respectively. Figure 19a shows the large -10 +20 mesh grains embedded in a matrix of slip-cast fused silica. From this photo and from the casting behavior of the mix, it appears that the large grains are nearly in contact. The surface of the large grains are typical of the as milled surface and higher magnification (Figure 19b) shows a thin layer of slip particles adhering to the surface of the coarse aggregate. Careful inspection shows that the coarser slip particles are not bonded to the large grain, while both Figures 19b and 19c indicate that the slip-cast fused silica matrix is highly sintered. All of these photos suggest that the -10 +20 mesh aggregate material failed through intergranular fracture of the matrix.

Figures 20a and 20b show a similar situation although several of the aggregate grains show a conchoidal fracture indicating intragranular fracture, at least of the coarse grains. Again the matrix seems to have failed through intergranular fracture.

In Figures 21a and b, it can be seen that the larger slip particles and smaller aggregate particles are indistinguishable. Both pictures, particularly the higher magnification show included porosity, both in the vicinity of the largest grains and along grain boundaries.
Figure 17. Dynamic Young's Modulus versus Bulk Density for High Purity Aggregate Cast Fused Silica
Figure 18. Dynamic Young's Modulus versus Modulus of Rupture for High Purity Aggregate Cast Fused Silica
Figure 19. Scanning Electron Micrographs of Fracture Surface of High Purity Aggregate Cast Fused Silica with 50 w/o -10 + 20 Mesh Grain
Figure 20. Scanning Electron Micrograph of Fracture Surface of High Purity Aggregate Cast Fused Silica with 50 w/o -20 + 50 Mesh Grain
Figure 21. Scanning Electron Micrograph of High Purity Aggregate Cast Fused Silica with 50 w/o -50 Mesh Grain
of the smaller grains. Here the presence of large areas where grains have been fused together and subsequently fractured shows intragranular fracture although equal areas of intergranular fracture are also present.

The same features are seen in Figures 22a and b, the slip-cast fused silica sample. Here intragranular fracture can be seen in Figure 22b, particularly in the lower center where grain boundary porosity is present on the fracture surface. The other "rock pile" areas characteristic of lower density slip-cast fused silica, indicate widespread intergranular fracture also.

The overall impression is that the matrix particularly in Figures 20, 21 and 22, fails in both intragranular failure. Previously published scanning electron micrographs show that for slip-cast fused silica, all intragranular fracture occurs only at extremes of sintering [7/]. In this case sintering has not reached that stage in all areas of the matrix. The -10 +20 mesh grains appear to pull out on fracture, while the -20 +50 mesh grains in some cases appear to be bonded to the matrix to fracture themselves. It is suspected that this merely results from the matrix having surrounded an elongate particle, and has little to do with the actual bonding of the slip and aggregate particles; i.e., the aggregate particles are caged but not necessarily bonded to the matrix. No conclusions can be made about the failure mode of the -50 mesh grains.

D. Evaluation of High Purity, Aggregate Cast Fused Silica

Four aggregate cast compositions were selected for comparison with slip-cast fused silica. These were the three previously studied compositions and a fourth with a composition of 65 percent slip, percent -50 mesh grain. The latter was selected in an effort to maximize specific surface and cast bulk density for the material. It was felt that a lesser amount of grain would be difficult to keep in
Figure 22. Scanning Electron Micrograph of High Purity Slip-Cast Fused Silica
suspension. Samples were cast as before with the slip-cast fused silica samples cast as 3/4 diameter x 6-inch circular bars. Aggregate cast samples were sintered 70 minutes at 2400° F to obtain a density just short of maximum, while the slip-cast fused silica bars were sintered six hours at 2200° F an optimal sintering time for that particular slip. The sintered samples were evaluated for bulk density, porosity, specific gravity, dynamic Young's modulus, and modulus of rupture. Dielectric specimens were machined from samples of the three 50/50 slip/grain compositions, and a pair of bars from each of these compositions was evaluated for creep rate and modulus of rupture after creep at 2000° F. Physical and mechanical property data for these specimens are shown in Table IX and dielectric properties in Table X. Dynamic Young's modulus data from Table IX appears to be strictly a function of density and are in good agreement with prior history of elastic modulus versus density for slip-cast fused silica as shown in Figure 4-2 of Reference 8/. The values for dielectric constant in Table X are in good agreement with previous values obtained for slip-cast fused silica if the values for density from Table IX are used instead of the values in Table X. Table IX values for bulk density were obtained using ASTM C373 while Table X values are calculated from weight and length, width and depth measurements. The dielectric constant for the -20 +50 mesh grain sample falls slightly below the average line of Figure 4-23 of Reference 8/. However, the other two samples measured fall very close to the line. The somewhat higher than normal values for loss tangent are believed to be due to insufficient drying of the samples before measurement.

The major difference in the aggregate cast specimens and slip-cast fused silica is in the modulus of rupture which cannot be related to density. Modulus of rupture is directly related to the degree of sintering, with more sintering occurring with the finer grain materials.
<table>
<thead>
<tr>
<th>Percent Grain Size</th>
<th>Bulk Density ($gm/cm^3$)</th>
<th>Porosity (%)</th>
<th>Specific Gravity ($gm/cm^3$)</th>
<th>Dynamic Young's Modulus ($10^6$ psi)</th>
<th>Modulus of Rupture (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 -10 +20</td>
<td>2.026 ± 0.004</td>
<td>8.19 ± 0.23</td>
<td>2.206 ± 0.004</td>
<td>5.85 ± 0.20</td>
<td>1305 ± 378</td>
</tr>
<tr>
<td>50 -20 +50</td>
<td>1.869 ± 0.012</td>
<td>14.29 ± 0.54</td>
<td>2.181 ± 0.002</td>
<td>4.12 ± 0.26</td>
<td>1499 ± 187</td>
</tr>
<tr>
<td>50 -50</td>
<td>1.896 ± 0.006</td>
<td>12.00 ± 0.32</td>
<td>2.155 ± 0.004</td>
<td>5.10 ± 0.18</td>
<td>2570 ± 269</td>
</tr>
<tr>
<td>35 -50</td>
<td>2.021 ± 0.003</td>
<td>6.09 ± 0.13</td>
<td>2.152 ± 0.001</td>
<td>6.82 ± 0.13</td>
<td>2866 ± 427</td>
</tr>
<tr>
<td>0 HP Slip</td>
<td>1.951 ± 0.002</td>
<td>10.73 ± 0.18</td>
<td>2.186 ± 0.000</td>
<td>5.73 ± 0.08</td>
<td>5271 ± 360</td>
</tr>
</tbody>
</table>

Note: Aggregate samples sintered 70 minutes at 2400°F. HP slip sintered 6 hours at 2200°F. Confidence interval at 95 percent on Student T Distribution.
TABLE X
ROOM TEMPERATURE DIELECTRIC PROPERTIES OF FINAL SINTERED COMPOSITIONS OF HIGH PURITY AGGREGATE CAST FUSED SILICA

<table>
<thead>
<tr>
<th>Percent Grain Size</th>
<th>Bulk Density</th>
<th>Dielectric Constant (k')</th>
<th>Loss Tangent (tanδ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 -10 +20</td>
<td>2.046</td>
<td>3.47</td>
<td>0.005</td>
</tr>
<tr>
<td>50 -20 +50</td>
<td>1.876</td>
<td>3.15</td>
<td>0.003</td>
</tr>
<tr>
<td>50 -50</td>
<td>1.972</td>
<td>3.25</td>
<td>0.005</td>
</tr>
</tbody>
</table>

The best modulus of rupture obtained for the aggregate cast samples was only 54 percent of that for optimally sintered slip-cast fused silica.

A comparison of creep characteristics between the aggregate cast specimens and slip-cast fused silica was made by transversely loading specimens in three point bending at 2000°F. Deflection versus time for a transverse loading of approximately 2900 psi for each of the aggregate compositions and for slip-cast fused silica are shown in Figure 23. The only explanation for the greater creep rate of the aggregate castings made with -50 mesh grain is that these castings had a somewhat lower density than the other specimens. The limited creep data obtained indicates that there is very little difference in creep rate for specimens of the same density regardless of the size distribution of aggregate or the lack of aggregate in the case of the slip-cast material. The specimens were finally loaded to failure and hot modulus of rupture values for each composition are shown in Table XI.
Figure 23. Deflection versus Time for High Purity Aggregate and Slip-Cast Fused Silica (2900 psi Transverse Loading at 2000°F)
### TABLE XI
MODULUS OF RUPTURE OF AGGREGATE CAST SPECIMENS AT 2000° F

<table>
<thead>
<tr>
<th>Percent Grain</th>
<th>Grain Size</th>
<th>Bulk Density ((\text{gm/cm}^3))</th>
<th>Modulus of Rupture ((\text{psi}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>-10 +20</td>
<td>2.02</td>
<td>3639</td>
</tr>
<tr>
<td>50</td>
<td>-20 +50</td>
<td>1.91, 1.92</td>
<td>3592, &gt; 4030*</td>
</tr>
<tr>
<td>50</td>
<td>-50</td>
<td>1.84, 1.84</td>
<td>3315, &gt; 4175*</td>
</tr>
<tr>
<td>0</td>
<td>HP Slip</td>
<td>1.95</td>
<td>&gt; 7020*</td>
</tr>
</tbody>
</table>

*Load limit of 285 pounds applied to specimens without failure.

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**E. Improvement in Sintering of Large Grain High Purity Aggregate Cast Silica**

An effort was made to increase the surface activity of the high purity aggregate by selectively etching the surface of the grains in hydrofluoric acid. Microscopic examination of individual grains before and after treatment indicated that the grains were uniformly decreased in size with no indication of selective etching. Because of time and fund limitations it was not possible to etch sufficient grain to produce test bars.
IV. CONCLUSIONS

1. Aggregate casting of fused silica can be used as an alternate method of fabrication to slip casting.

2. The degree of drying shrinkage can be greatly reduced and the cast density greatly increased using aggregate casting in preference to slip casting.

3. The cast density increases as aggregate particle size increases and hence casting shrinkage decreases.

4. The amount of sintering densification (shrinkage) decreases as aggregate particle size increases.

5. High purity aggregate and slip materials can be densified more by sintering than can technical grade materials.

6. Density dependent properties such as elastic modulus and dielectric constant of aggregate cast specimens give equivalent values to slip-cast fused silica.

7. Properties dependent on the degree of sintering such as modulus of rupture are much lower for aggregate cast material than slip-cast fused silica.

8. Aggregate cast material can be machined, but greater care is required than with slip-cast fused silica to avoid grain pull-out.

9. The selection of grain size and percentage will influence as cast and sintered physical and mechanical properties. Hence, the selection of a composition for aggregate casting will depend on the final desired properties.

10. Aggregate casting can replace slip casting for the manufacture of fused silica shapes to close tolerances with very little shrinkage in casting or firing. However, present compositions will have considerably less transverse strength than slip-cast fused silica.
V. RECOMMENDATIONS

The transverse strength values for the aggregate cast fused silica were considerably lower than those for slip-cast fused silica and strength decreased with increasing size of aggregate. The modulus of rupture values using -10 +20 mesh material were no better using high purity material than using commercial grade material. However, for -20 +50 mesh material there was a definite increase in strength using the high purity material due to increased sintering.

The current high purity fused silica material both aggregate and slip, is prepared by milling in alumina ball mills with alumina media. Some alumina contamination occurs and is not completely removed by acid leaching. The high purity slip cannot be leached without changing the particle size dispersion. A much purer silica and hence more active particles could be obtained by milling in high purity fused silica mills and utilizing high purity fused silica grinding media. The material ground in this manner should be much more active and considerably more sintering should occur even with particles in the -10 +20 mesh size range.

A similar study to the high purity portion of this program should be conducted to determine the physical and mechanical properties of aggregate cast material prepared in fused silica mills. Some slight changes in compositions may be required because of differences in rheology of a very high purity fused silica slip. If this study shows a large improvement in transverse strength properties of sintered materials then efforts should be made to develop techniques for aggregate casting radome shapes and diamond grinding of these shapes for final finishing and electrical tailoring.
REFERENCES


This program investigated aggregate casting of fused silica as a means of reducing drying and sintering shrinkage in the production of slip-cast fused silica. The efficiency of particle packing was increased so that green bulk densities greater than 2.0 gm/cm\(^3\) were achieved. Drying shrinkage was reduced to essentially zero. Sintered properties dependent on bulk density such as dynamic elastic modulus and dielectric constant had the same values as slip-cast fused silica of the same density. Transverse strength which is dependent on the degree of sintering ranged from 25 to 60 percent as strong as slip-cast fused silica of 1.95 gm/cm\(^3\) density. Transverse strength decreased as aggregate particle size increased. Methods for increasing this strength would be to obtain a more active aggregate by eliminating surface impurities or to decrease the mean particle size of the starting materials both slip and aggregate. Surface grinding was limited to machining of dielectric specimens, but no problems were encountered with grain pull out.
Fused Silica:
  Slip-Cast
Aggregate Cast
  Drying
  Sintering
Physical Properties
Mechanical Properties
Dielectric Properties