FUSED SILICA MANUAL

BY

JULIAN D. FLEMING

AND OTHERS

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ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

PROGRESS REPORT NO. 1

Project No. B-153

FUSED SILICA FOR REACTOR APPLICATIONS

By

J. D. FLEMING AND J. W. JOHNSON

CONTRACT NO. AT-(40-1)-2483
U. S. ATOMIC ENERGY COMMISSION

14 NOVEMBER 1958 TO 15 AUGUST 1959

Engineering Experiment Station
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FOREWORD

The investigation covered in this report was performed by the Engineering Experiment Station of the Georgia Institute of Technology under AEC Contract No. AT-(40-1)-2483. This contract was administered by the Oak Ridge Operations Office of the U. S. Atomic Energy Commission, Reactor Division, Dr. David F. Cope, Director.

The first progress report covers the period of work from 14 November 1958 to 15 August 1959.
# Progress Report No. 1, Project No. B-153

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I. INTRODUCTION

The excellent thermal shock resistance and preliminary indications of good resistance to radiation damage of fused silica have recommended it for consideration for use in high temperature radiation fields. With the development at Georgia Tech of techniques for economical fabrication of large and complex silica shapes by slip casting, major objections to this material, on the basis of cost and fabrication difficulty, have been overcome.

Although the art of fused silica is well developed, its science is in its infancy. Insufficient data are available for the intelligent evaluation of fused silica as a reactor material. The object of Project No. B-153, AEC Contract AT-(40-1)-2483, is the development of sufficient reliable data for, and basic understanding of, fused silica to permit this evaluation.

This report covers the initial exploratory investigations designed to define the areas in which data are required for fused silica, the techniques developed for determining these data, and the first results of these determinations.
II. SUMMARY

Adequate definition of the silica system to be considered was accomplished. This system was a slip of amorphous silica in water, with a total metallic impurity content of 0.12 per cent and a particle size distribution with 90 per cent less than 35 microns and 10 per cent less than 0.9 micron, and fired bodies cast from this slip.

Techniques were developed for determining the tensile strength of the slip cast fused silica from room temperature to 1800°F. These strengths were of the order of 1500 psi at room temperature and 3400 psi at 1800°F. Studies were begun to extend the testing temperature range above 2100°F.

The variation of modulus of rupture of the slip cast fused silica with firing conditions was investigated. Moduli of rupture ranged from about 1200 psi, for bodies fired at 2000°F for 2 hours, to about 6500 psi for bodies fired at 2300°F for 1/2 hour. Concomitant changes in the porosity, surface area, and cristobalite content were determined.

A technique for the determination of permeation coefficients for gas flow through the silica was developed using tracer techniques. A system, based on this technique, was constructed for use at room temperature and evaluated using radio-krypton permeation of unsealed, slip cast fused silica. Tentative experiments indicated the permeation coefficient, or effective diffusivity, for this system to be of the order of $10^{-2} \text{ ft}^2/\text{hr}$. Studies were begun, using this technique, to evaluate the effectiveness of various suggested methods of sealing the porous silica.

Basic x-ray diffraction techniques were applied to the analysis of silica for cristobalite content. A platinum wound furnace was designed and constructed to allow dynamic observations of the crystallization of cristobalite in fused silica at elevated temperatures. Based on the analytical procedures established,
the bulk growth rates of cristobalite, in the silica system studied, was about one per cent per hour at temperatures in the range of 2100°F. Surface growth rates were grossly in excess of this figure, probably because of a higher concentration of small silica particles at the surface of the cast specimen.

Studies were initiated in the fields of optical and electron microscopy and selected area electron diffraction to determine the nature of the cast silica microstructure. These studies were pointed toward explanation of the mechanics of particle bonding in the slip cast fused silica and investigations of the kinetics of this bonding process.

Procedures were developed for casting simple, single piece shell and tube heat exchangers of fused silica. These exchangers were subjected to elementary heat transfer tests.

An irradiation experiment was designed for inclusion in the first testing cycle of the Westinghouse Testing Reactor. This study will serve to make a preliminary, exploratory evaluation of the physical effects of fast neutron damage in fused silica.
III. EXPERIMENTAL WORK

A. Initial Screening Studies

A list of variables which would be expected to influence the properties of fired fused silica bodies would be quite long. Of these variables, however, three classes would seem to be of major importance:

1. Nature of the slip -
   - Particle size
   - Viscosity
   - pH

2. Fabrication technique -
   - Mold shape and mass
   - Mold permeability
   - Casting time
   - Drying time and temperature

3. Firing conditions -
   - Firing time
   - Firing temperature
   - Furnace atmosphere

Casual consideration of these variables will indicate that the influence of the firing conditions could be more easily predicted and that these conditions could be controlled and bracketed with a greater degree of assurance than the other two classes of variables. With this in mind, the decision was made to fix, as well as possible, the nature of the slip and the fabrication technique and to investigate the effect of the firing conditions on the properties of slip cast silica bodies. The background gained in this investigation could then be utilized in more intelligent planning of experiments to investigate the other variables.
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1. Experimental Work.--

Three fused silica slips, differing primarily in particle size, were obtained from the Glasrock Products Corporation of Atlanta which has facilities for producing these materials in large quantities. The particle sizes of these slips were measured by conventional sedimentation techniques and are summarized in Table I.

**TABLE I**

PARTICLE SIZE SUMMARY FOR TEST SLIPS

<table>
<thead>
<tr>
<th>Slip No.</th>
<th>90 Per Cent of Particles Less Than (Microns)</th>
<th>10 Per Cent of Particles Less Than (Microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>34</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>1.3</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>0.9</td>
</tr>
</tbody>
</table>

*Extrapolated

In order to make a brief qualitative determination of the influence of particle size on the fired strength of the cast silica, tensile tests were made using both Stoddard and B sample configurations, discussed in the tensile testing section to follow. The tensile bars were fired in a gas combustion kiln at approximately 2050°F for two hours. The average tensile strengths for bars cast from the three test slips are shown in Table II. As may be seen from Table II, the fired tensile strength increased for decreasing particle size.
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TABLE II
TENSILE STRENGTHS OF TEST SLIPS

<table>
<thead>
<tr>
<th>Slip No.</th>
<th>Tensile Strength (PSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1400</td>
</tr>
<tr>
<td>2</td>
<td>668</td>
</tr>
<tr>
<td>3</td>
<td>1630</td>
</tr>
</tbody>
</table>

Based on the results shown in Table II, Slip No. 3 was selected as the standard to be used in the initial studies. A uniform 100 gallon quantity of this slip was milled by the Glasrock Products Corporation and thoroughly tested. The particle size distribution of this slip is shown in Figure 1. The slip viscosity was 131 cp., the pH was 5.2 and the solids content was 81.6 per cent. Semi-quantitative emission spectrography showed the slip to have the analysis shown in Table III.

TABLE III
METALLIC IMPURITIES IN STANDARD SLIP

<table>
<thead>
<tr>
<th>Element</th>
<th>Approximate Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.001</td>
</tr>
<tr>
<td>Fe</td>
<td>0.008</td>
</tr>
<tr>
<td>Al</td>
<td>0.008</td>
</tr>
<tr>
<td>Cu</td>
<td>0.04</td>
</tr>
<tr>
<td>Ag</td>
<td>0.0003</td>
</tr>
<tr>
<td>Ti</td>
<td>0.001</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0003</td>
</tr>
<tr>
<td>Ca</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Total maximum metallic impurities = 0.12 per cent
Figure 1. Particle Size Distribution for Standard Slip.
All data and discussion in the remainder of this report refer to the standard slip unless otherwise noted.

B. Tensile Strength Determinations

1. Equipment.--

All tensile tests were carried out on a Dillon Model L Universal Tester using certified calibrated dynamometers of 250, 500, and 1000 pound capacities. A crosshead speed of 0.125 in. per minute was selected giving strain rates of approximately 0.015 in. per in. per minute.

2. Experimental Work.--

Based on a survey of the literature on photoelastic studies of tensile test specimen configurations, a design similar to that of Stoddard\(^1\) was chosen for the silica samples. Split aluminum master molds were machined from which plaster molds were cast. The molds were coated with Keltex release compound and filled with silica slip to cast the Stoddard specimens. An aluminum master, a plaster mold, and a cast Stoddard bar are shown in Figure 2. After thorough drying at about 200\(^0\)F, the bars were fired at approximately 2050\(^0\)F in a gas combustion furnace for two hours. Upon testing these samples, it was found that the abrupt change in cross section caused a high percentage of the samples to break at the conical end.

In order to decrease the stress concentration at the holding ends, a specimen, designated B, was designed using a more gradual area change. Figure 3 shows an aluminum master, a plaster mold, and a cast B specimen. Specimens were prepared and fired as stated above.

\(^1\)Stoddard and Allison, Bul. Am. Ceram. Soc. 37 No. 9 409-413 (1958)
Figure 2. Molds and Cast Stoddard Tensile Test Specimen.
Figure 3. Molds and Cast B Tensile Test Specimen.
A series of B tensile samples was fabricated and tested in order to determine the reproducibility of results obtained with the new configuration. For 37 samples cast from Slip No. 3, the average tensile strength was 1630 psi plus 40.5 per cent minus 34.0 per cent with an average deviation of 15.2 per cent. This reproducibility was thought quite satisfactory, especially in view of the fact that firing in the gas kiln lent only poor temperature control. The B configuration was used for all further room temperature tests.

Two concurrent programs were begun to investigate the tensile properties of slip cast fused silica. In the first, the influence of firing temperature and firing time on the tensile strength was studied. Test specimens were fabricated and fired in a Globar tube furnace using different combinations of time and temperature. The Globar furnace allowed closer firing temperature control. At a specified temperature, indicated on the furnace control, a temperature profile was obtained using a thermocouple placed at measured positions in the tube. From the temperature profile, the firing temperature of articles in the tube could be reliably estimated. The variation of tensile strength with firing conditions is shown in Figure 4 for the conditions initially studied.

The second tensile test program was pointed toward the determination of the tensile properties of slip cast fused silica at elevated temperatures. In the initial stages of this investigation, a series of B tensile bars was fabricated and fired for two hours at approximately 2100°F in the gas combustion kiln. The central portion of the fired test bar was heated using a tubular resistance heater and its temperature was measured both optically and with a thermocouple incorporated in the furnace. The bar was broken under tension after thermal equilibrium was attained.
Figure 4. Tensile Strength of Cast Fused Silica as a Function of Firing Time at 2200°F.
At lower testing temperatures, the system using B specimens performed satisfactorily. As the testing temperature increased, however, the rapid increase in the tensile strength of the hot zone caused the specimen to break in the cold zone. This cold zone break occurred even though the cross sectional area of the sample at that point was greater than the hot zone area by a factor of at least two. As the testing temperature reached 1800°F, approximately 75 per cent of the samples tested failed in the cold zone.

In order to overcome the cold zone fracture, the ends of the test bars were soaked in phenolic resins and in hydrolyzed ethyl silicate. Since none of these treatments increased the cold zone strength by more than 100 per cent, this attempt met with little success.

Two further methods of obtaining reliable elevated temperature data were considered. The first was testing, under compression, a silica ring of a configuration which would undergo pure tensile fracture at predicted positions. This test has been extensively investigated at the Armour Research Foundation. Its use would require construction of a new test facility. Design of this facility was begun.

The second alternative was testing a conventional specimen heated throughout its length. Inconel holding fixtures of a design being used by ORNL were obtained from the Inco Investment Castings Company. Threaded tensile specimens were cast to fit these holders. An aluminum master, a plaster mold, and a cast specimen of this configuration are shown in Figure 5.

A series of threaded samples was fired and tested at temperatures of 1800° to 2000°F. These samples showed a tendency to crack at stress concentration points in the threads. Attempts were begun to eliminate thread cracking by using shallow threads.

Private communication from Mr. Sam Bradstreet.
Figure 5. Mold and Cast Threaded Tensile Test Specimen.
Figure 6 shows the tensile strength of fused silica as a function of testing temperature for the temperatures, using both B and threaded specimens, for which statistically reliable data were obtained. All samples tested in the preparation of Figure 6 were fired at $2100^\circ$F for two hours.

C. Firing Condition Studies

Measurement of the modulus of rupture of brittle materials is less subject to systematic error than tensile strength measurement. The modulus of rupture, therefore, was chosen as the correlation index for the initial studies of the influence of firing conditions on the strength of cast fused silica.

1. Equipment. --

All modulus of rupture measurements were made on a Dillon Model L Universal Tester. Certified calibrated dynamometers with capacities of 250, 500, and 1000 pounds were used. A crosshead speed of 0.125 in. per minute was employed.

2. Experimental Work.--

Brass master molds were machined in the form of split cylinders, 3/4 in. in diameter by six inches long and 3/8 in. in diameter by four inches long. Modulus of rupture specimens were cast in plaster molds made using the brass masters. The cast bars were dried at approximately $200^\circ$F preparatory to firing. All firings in this study were made in the Globar furnace described in the preceding section.

The first study of the firing conditions was carried out in such a way as to establish the ranges of importance for more detailed investigations. Several sets of bars, both 3/8 - and 3/4-inch diameter, were fired at temperatures of $2000^\circ$, $2100^\circ$, and $2200^\circ$F for times of 2, 4, 8, and 16 hours and at $2300^\circ$F for 1/2, 1, 2, and 4 hours. Each set of bars was made up of twenty 3/8-inch bars and twelve 3/4-inch bars.
Figure 6. Tensile Strength of Slip Cast Fused Silica as a Function of Temperature.
After the bars were broken, they were examined by x-ray diffraction to determine the cristobalite content and by nitrogen adsorption to measure the specific surface area. The porosity and density of the silica were determined as a function of the firing conditions by weighing the bars dry, weighing under water after boiling to remove the air and saturate the pores, and weighing the water-filled bars.

The strength of the cast silica was found to increase with firing temperature and time to a maximum and then decrease as shown in Figures 7 and 8. The average strengths of the 3/8- and 3/4-inch bars compared reasonably well as is shown for a typical series of firings in Table IV, although the smaller bars generally showed greater deviations from the average, as would be expected.

**TABLE IV**

COMPARISON OF MODULUS OF RUPTURE OF 3/8- AND 3/4-INCH DIAMETER SPECIMENS

<table>
<thead>
<tr>
<th>Firing Temperature (°F)</th>
<th>Firing Time (Hr)</th>
<th>MR of 3/8-Inch Bars (PSI)</th>
<th>Average Deviation (Per Cent)</th>
<th>MR of 3/4-Inch Bars (PSI)</th>
<th>Average Deviation (Per Cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>2</td>
<td>1300</td>
<td>18.0</td>
<td>1430</td>
<td>14.0</td>
</tr>
<tr>
<td>2000</td>
<td>4</td>
<td>3100</td>
<td>29.0</td>
<td>3350</td>
<td>12.2</td>
</tr>
<tr>
<td>2000</td>
<td>8</td>
<td>4000</td>
<td>20.1</td>
<td>4430</td>
<td>8.6</td>
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<tr>
<td>2000</td>
<td>16</td>
<td>3730</td>
<td>15.7</td>
<td>3290</td>
<td>17.0</td>
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<tr>
<td>2100</td>
<td>2</td>
<td>2480</td>
<td>15.8</td>
<td>2770</td>
<td>14.1</td>
</tr>
<tr>
<td>2100</td>
<td>4</td>
<td>2810</td>
<td>19.7</td>
<td>2870</td>
<td>15.2</td>
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<tr>
<td>2100</td>
<td>8</td>
<td>4580</td>
<td>12.1</td>
<td>3980</td>
<td>17.7</td>
</tr>
<tr>
<td>2100</td>
<td>16</td>
<td>3780</td>
<td>17.5</td>
<td>3820</td>
<td>10.9</td>
</tr>
</tbody>
</table>
Figure 7. Modulus of Rupture of Slip Cast Fused Silica as a Function of Firing Temperature at Constant Firing Time.
Figure 8. Modulus of Rupture of Slip Cast Fused Silica as a Function of Firing Time at Constant Firing Temperature.
The x-ray analysis showed small bulk percentages of cristobalite to be present in the bars. The percentage of cristobalite increased with firing temperature and firing time. This increase approximated a linear function of time as is seen in Figure 9. The method of cristobalite analysis and the error involved is treated in the section on devitrification to follow.

The porosity of the fired cast silica decreased with increasing firing temperature and time as is shown in Figure 10. Since the scatter of the data was, in most cases, so great, little quantitative significance could be attached to the trend noted.

The specific surface area of the fired silica was also found to decrease with increasing firing temperature and time but not in a manner which could be correlated with firing conditions. The average specific surface areas are shown in Table V. Since the estimated error in the surface area determinations could not account for the data scatter noted, efforts were begun to determine the reason for this anomalous behavior through systematic firing studies.

**TABLE V**

**SPECIFIC SURFACE AREAS OF FUSED SILICA**

<table>
<thead>
<tr>
<th>Firing Temperature (°F)</th>
<th>Firing Time (Hr)</th>
<th>*Specific Surface Area (M²/Gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>2</td>
<td>2.74</td>
</tr>
<tr>
<td>2000</td>
<td>4</td>
<td>2.48</td>
</tr>
<tr>
<td>2000</td>
<td>8</td>
<td>1.04</td>
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<tr>
<td>2000</td>
<td>16</td>
<td>1.09</td>
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<tr>
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<td>2</td>
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<td>2.31</td>
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<tr>
<td>2100</td>
<td>16</td>
<td>2.85</td>
</tr>
</tbody>
</table>

(Continued)
Figure 9. Bulk Growth of Cristobalite in Modulus of Rupture Specimens.
Figure 10. Porosity of Cast Silica as a Function of Firing Conditions.
D. Permeation Studies

For evaluation of the application of slip cast fused silica to nuclear engineering materials problems, data on the gas tightness of fired bodies are essential. Both high temperature heat exchanger design and fuel element matrices, for example, require knowledge of gas retention capability.

With the dual objects of developing a versatile, convenient and reasonably accurate system and a system which would use a minimum of instrumentation, a permeation apparatus employing a radioactive tracer gas was designed. In addition to satisfying the above criteria, such a system with appropriate containment modification could operate at any chosen temperature since no withdrawal of gas for analysis would be required.
1. Equipment.--

A schematic diagram of the permeation system developed for room temperature use is shown in Figure 11. Figure 12 shows an overall view of the system. The test sample was clamped between two 2-in. Pyrex pipe crosses, one of which initially contained a radioactive tracer gas. Conventional counting equipment was used to measure the activity in each cross. In most of the experiments, the hot-side* activity was measured periodically with a Nuclear Chicago Model 181-A decade scaler. The cold-side activity was continuously recorded on a Wheelco Model 8000 recorder using the output signal from a Nuclear Chicago Model 1620A analytical count-rate meter. The permeation apparatus was contained in a chemical hood which was continuously monitored with a Nuclear Chicago Model 1619 Labitron count-rate meter. Nuclear Chicago Model D-33 end window Geiger tubes were used in all the counting equipment.

2. Experimental Procedure.--

Approximately 3 mc. of tracer gas was introduced into the hot-side Pyrex cross and the total pressure in the cross was adjusted to one atmosphere, the same pressure as that in the cold-side cross.

The tracer gas activity in a cross would be proportional to the number of tracer gas molecules in the cross, so that

\[ a = C_1 n \]  

(1)

where \( a \) represents the activity in the cross, \( n \) represents the number of moles of tracer gas in that cross, and \( C_1 \) is a proportionality constant. Since, in the system used, the counting geometry and counting system characteristics were known to be the same for both crosses, the same proportionality constant would apply to both the hot side and the cold side.

*In this discussion, hot and cold are used to describe the relative level of radioactivity rather than thermal activity.
Figure 11. Schematic Diagram of Room Temperature Permeation System.
Figure 12. Permeation System.
The rate of flow of tracer gas per unit area of sample surface exposed to
the permeating gas was assumed to bear a simple probability relation to the
difference in the numbers of gas molecules striking the hot and cold sides of the
sample and an inverse relation to the sample thickness. In engineering terms,
this statement may be represented by the relation

\[ G = \frac{kA}{L} (x_H - x_C) \]  

where \( G \) represents the net molar flow of tracer gas from the hot cross to the
cold cross, \( x \) represents the molar concentration of tracer gas in the cross,
subscript \( H \) refers to the hot cross, subscript \( C \) refers to the cold cross, \( k \)
represents the permeation coefficient, \( A \) represents the sample area perpendicular
to the direction of gas flow, and \( L \) represents the sample thickness.

Since

\[ G = \frac{dn_C}{dt} \]  

where \( t \) represents time, Equation 2 may also be written

\[ \frac{dn_C}{dt} = \frac{kA}{L} (x_H - x_C). \]  

Writing Equation 1 for the cold cross and differentiating with respect to time
yields

\[ \frac{da_C}{dt} = C_1 \frac{dn_C}{dt}. \]  

Also from Equation 1, since

\[ x = \frac{n}{V} \]

Where \( V \) represents the volume of the cross,

\[ x = \frac{a}{C_1 V}. \]  

Substituting Equations 5 and 6 into Equation 4 gives

\[ \frac{da_C}{dt} = C_1 \frac{kA}{L} \left( \frac{a_H}{C_1 V_H} - \frac{a_C}{C_1 V_C} \right) \]
or, since the cross volumes were equal,

\[
\frac{d\alpha_c}{dt} = \frac{kA}{LV} (a_h - a_c)
\]  

Equation 7 indicates that plotting the slope of the curve of cold-side activity versus time as a function of the difference in hot- and cold-side activities should yield a straight line whose slope would allow calculation of the permeation constant defined by Equation 2.

It is of interest to note that this method does not require knowledge of the specific activity of the permeating gas as many other tracer permeation experiments do. If, as would be expected, the background radiation is the same at both counting tubes, no background correction is required. This results from the fact that background cancels in the activity difference expression and does not appear in the differential activity change term.

3. Experimental Work.--

The majority of the experimental work during the report period was devoted to a practical evaluation of the validity of the above procedure. A series of silica discs, 3 in. in diameter and 1/4-in. thick, was fabricated. After being fired, a disc was clamped in the system, using overplasticized polyvinyl chloride gaskets, and subjected to permeation by krypton 85 as described above.

Figures 13 and 14 show the hot- and cold-side activities as a function of time for a typical run on a disc fired at 2200°F for four hours. Graphical differentiation of Figure 14 gave the plot of differential activity change as a function of time shown in Figure 15. Figure 16 illustrates the relationship between this differential activity change and the difference in hot- and cold-side activities. As Equation 7 predicts, the relation is seen to be linear and passes through the origin. For this run, the permeation coefficient is given by
Figure 13. Hot Side Activity as a Function of Time.
Figure 14. Cold Side Activity as a Function of Time.
Figure 15. Differential Cold Side Activity Change as a Function of Time.
Figure 16. Differential Cold Side Activity Change as a Function of Activity Difference.
\[ k = \text{slope} \times \frac{LV}{A} \]
\[ = 0.102 \text{ hr}^{-1} \left( \frac{0.25 \text{ in} \times 46 \text{ in}^3}{0.786 \text{ in}^2} \times \frac{1 \text{ ft}^2}{144 \text{ in}^2} \right) \]
\[ = 1.04 \times 10^{-2} \text{ ft}^2/\text{hr} \]

A series of investigations was begun to correlate the permeation coefficient for krypton flow through fused silica with the conditions used in firing the silica. Although the investigations have not yet been carried to the point of quantitative correlations, the trend shown in Figure 17 was noted.

Parallel studies were begun to determine the effectiveness of various techniques in sealing the porous cast silica. Techniques being investigated are soaking the silica in tetraethyl orthosilicate and Union Carbide Ethyl Silicate 40 and firing to deposit silica, soaking in alkaline aluminum phosphate to produce phosphate-silicate bonds, and flame glazing.

E. Devitrification Studies

Amorphous, or fused, silica is known to undergo devitrification, or crystallization, when heated to temperatures in the range of 2000°F. The major ordered crystal form resulting from the transformation of the metastable fused silica is cristobalite. Primarily because of the inversion of cristobalite at about 600°F, with the large concomitant specific volume change, this crystal form of silica is unable to withstand thermal shock. Prolonged heating of fused silica thus transforms it from a material with exceptional resistance to thermal shock to a material with little such resistance.

Initial studies of the strength of slip cast fused silica as related to firing conditions also showed a strong dependence on cristobalite formation. Formation of a suitable cast silica bond, therefore, requires a balance of increased strength with decreased thermal shock resistance, both resulting from cristobalite formation. For this reason, emphasis was placed on developing
Figure 17. Permeation Coefficient for Krypton Flow Through Silica Fired at 2200°F.
x-ray techniques suitable for diffraction studies of the kinetics of the crystallization of fused silica.

1. Equipment.--

The basic diffraction equipment used was a Norelco x-ray generator, with current stabilization, a Norelco diffractometer, Geiger counter sensed, and a binary scaler equipped with the proper circuitry to supply a count-rate pulse to a Minneapolis-Honeywell strip chart recorder incorporating a diffraction angle index.

For elevated temperature diffraction studies, use was made of an aluminum housing fitted with a sample furnace. Power to the electrically heated furnace was supplied by a Variac. The sample temperature was determined with a platinum thermocouple whose output was measured both with a Leeds and Northrup potentiometer and a calibrated Wheelco Model 403 controller which also regulated the power input to the furnace. As protection for the high temperature system, a hydrostatic relay was incorporated in the exhaust of the coolant stream to the high temperature unit. In the event of coolant line failure, the relay would completely shut down all components of the system.

2. Experimental Work.--

In order to furnish a basis for the quantitative x-ray analysis of the cristobalite content of the partially devitrified slip, steps were first taken to form a completely crystallized sample of silica. A quantity of cast slip was heated at 2400°F for 48 hours. This sample was examined according to established x-ray diffraction procedure, using copper Kα radiation, with observations being made of the peaks of cristobalite at 2θ angles of 22 and 36.5 degrees. The crystallinity of the sample, designated A3, obtained by integrating these peaks was found to be equal to that of cristobalite samples obtained from the Bureau of Standards and U. S. Steel which were examined in the same way. In view of this correlation, A3 was accepted as the standard for all cristobalite analyses.
Using mechanical mixtures of A3 and amorphous silica, calibration curves were prepared to allow quantitative analysis for cristobalite content. At low concentrations of cristobalite, the crystalline phase is known not to be completely ordered. As a result, analyses which would concretely yield the total amounts of ordered and disordered cristobalite are clearly impossible. With this in mind, it was decided that the results of the x-ray analyses would be stated, on the basis of the aforementioned calibration curves, in terms of equivalent highly ordered crystallinity. In the interests of simplicity, these results were called merely per cent cristobalite. In this report, it should be clearly understood that these compositions represent only the equivalent percentage of ordered cristobalite, mixed with completely disordered fused silica, required to give the same peak area as that noted in the x-ray analysis.

Having generated the calibration curves, the next step taken was the development of suitable standard procedures for room temperature x-ray diffraction analyses for cristobalite content. After extensive study, the conclusion was drawn that small percentages of cristobalite, below about 10 per cent, could best be detected by measurement of the area of the Α- cristobalite peak at a 2θ angle of 22 degrees which is superimposed on the amorphous silica hump. Above about 10 per cent cristobalite, best results were obtained from integrating the Α- cristobalite peak at a 2θ angle of 36.5 degrees. Estimated absolute errors for this technique were 0.25 per cent below 10 per cent cristobalite and one per cent above this point. Cristobalite contents below about one per cent could be estimated only as to order of magnitude.

In preparation for the determination of devitrification rates by dynamic rate studies, a program was initiated to develop a stable, uniformly heated furnace for the high temperature camera. Furnaces were first constructed along
conventional lines using a single Globar over which the sample tray was suspended. This technique, at least for the low conductivity silica, proved unsatisfactory. Temperature gradients which could not be measured accurately were set up in the sample. As a result, the sample temperature over the infinite x-ray thickness was indeterminate.

In order to overcome this disadvantage, a furnace was designed which would heat the sample on all sides, thereby eliminating temperature gradients. A small refractory shell, 2 inches on a side with 1/4-inch walls was fabricated. Small windows were incorporated to admit the incident x-ray and to pass the diffracted beam. The first furnace prototype used internal coils of Kanthal mounted both at the top and bottom of the chamber. Alumina posts mounted in the furnace to hold a cast silica specimen 1 by 2 by 1/5-cm. in size. A thermocouple post was placed in very close proximity to the bottom of the sample.

The prototype furnace operated very satisfactorily in check runs to temperatures of about 2100°F but burned out above this point. A second furnace was constructed using the same design as the prototype, but with platinum rather than Kanthal coils. Details of the high temperature unit are shown in Figures 18, 19, 20, and 21, and a schematic diagram of the high temperature diffractometer attachment is shown in Figure 22. The diffraction system is shown in operation in Figure 23.

The platinum wound furnace was subjected to complete testing at temperatures up to 2300°F. The temperature could be easily controlled within 5°F with total furnace power requirements of less than 450 watts. No evidence of gross deterioration was noted during the test runs. A very small quantity of quartz and platinum from the furnace was found to deposit on the sample surface during the runs but, since it was felt that suitable corrections could be applied, this represented no source of major difficulty.
Figure 18. Back View of High Temperature Diffractometer Attachment.
Figure 19. Assembly View of High Temperature Diffractometer Attachment.
Figure 20. Front Detail of High Temperature Diffractometer Attachment.
Figure 21. Furnace Unit for High Temperature Diffractometer Attachment.
Figure 22. Schematic Diagram of High Temperature Diffractometer Attachment.
Figure 23. High Temperature Diffraction System in Operation.
Investigations were begun to outline the range of devitrification of the silica. Samples were cast as before from the standard slip and dried thoroughly. A sample was mounted in the x-ray camera and heated to the test temperature which was maintained by the Wheelco controller. Using copper $K_{\alpha}$ radiation, continuous scans were made through 2$\theta$ diffraction angles of 18.5 to 24.5 degrees. These scans were regulated by a reversing switch incorporated in the diffraction angle index. Following the high temperature run, the sample was analyzed at room temperature for the concentration of $\alpha$-cristobalite on the surface at which the temperature was measured. The sample was also crushed and analyzed for bulk cristobalite content.

Analysis of the data was carried out by determining the curve for the rate of crystallization from the relative peak areas found from the continuous high temperature run. The position of the rate curve on the cristobalite percentage axis was established by the final cristobalite percentage determined in the room temperature quantitative analysis.

For the temperatures for which tentative data have been completely analyzed, Figure 24 shows the cristobalite content in the surface of slip cast fused silica as a function of time.

Since cristobalite is known to grow from the surface of fused silica, and for reasons to be discussed later, concurrent studies were begun to determine the growth rate of cristobalite in the bulk of the silica. Samples were heated to known temperatures for known periods of time, quenched, crushed, and analyzed for cristobalite content. The results of these studies, to date, are shown in Figure 25.
Figure 24. Formation of Cristobalite on the Surface of Slip Cast Fused Silica.
Figure 25. Bulk Growth of Cristobalite in Slip Cast Fused Silica.
F. Microscopy

In order to establish a fundamental basis for evaluation of the properties of the slip cast fused silica, a program of optical and electron microscopy was begun. This, it is anticipated, would give a pore size, an indication of the distribution of particles and pores in the cast bars, and shed some light on the mechanism of bonding of the material.

1. Equipment.--

Conventional optical microscopes were employed, including a Bausch and Lomb Stereomicroscope for quick, low magnification and a Leitz Neophot metallurgical microscope and a Leitz medical microscope with ultra-pak attachments for higher magnifications.

An R.C.A. EMU-2 microscope was used in electron microscope studies and for selected area electron diffraction.

Various other equipment, such as a Syntron polisher and vacuum systems, was employed in the preparation and treatment of samples prior to examination.

2. Experimental Work.--

a. Optical Microscopy

As a result of very poor particle contrast, slip cast fused silica is a rather difficult subject for optical microscopy. Screening of a number of fluorescent materials was conducted to try to find a material with which the slip cast fused silica samples could be soaked, thus outlining pores so that the pore size and distribution might be determined. These studies were soon abandoned and this search continued with other conventional methods of optical and electron microscopy. Sample surfaces which were scribed and broken or sawed were mounted and polished and observed, as well as samples of as cast silica bodies.
The extreme whiteness and fine particle size of the slip cast fused silica left a great deal to be desired as far as contrast and resolution were concerned for the optical microscope. Several techniques were employed to improve this. The most successful were dyeing and shadowing, employed both separately and together.

The samples were dipped in a dye, such as methyl blue or blue writing ink which improved the contrast and definition. On samples such as the unpolished cast surfaces, and some of the polished ones, shadowing further enhanced the contrast and gave the sample some relief. Shadowing of the sample was accomplished by placing it in a vacuum chamber and evaporating a metal such as chromium onto the surface at an angle of 10 to 15 degrees to its plane axis. This technique produced a surface not nearly so bright as before and with the different planes easily discernible. A typical micrograph obtained in this way is shown in Figure 26.

b. Electron Microscopy and Diffraction

Surfaces for observation with the electron microscope and its diffraction attachments were prepared in a manner similar to that for optical microscopy. Replica techniques were primarily used for this type of microscopy, although the use of powder samples of ground and milled specimens of the slip cast fused silica was begun for transmission examination.

Plastic replicas, such as collodion, polyvinyl alchol, and polystyrene, and carbon replicas were used with the latter being most successful for microscopic examinations. A typical example is Figure 27. The preparation of electron stereo micrographs was begun in an attempt to facilitate interpretation of the structure. Studies utilizing electron diffraction were begun to examine the...
Figure 26. Optical Micrograph of Unfired Cast Fused Silica. (900x)
Figure 27. Electron Micrograph of Carbon-Platinum Replica of Cut Surface of Cast Fused Silica. (34,000x)
bonding mechanism between the particles of the slip cast fused silica. There appears to be a definite possibility that the selected area diffraction patterns of areas of these bonds may be revealed by examination of bonded silica particles stripped, along with plastic replicas, from the surface of a specimen. Initial progress with this technique showed promise of successful development.

G. Heat Exchanger Fabrication

1. Experimental Work.--

Although final production of a useable fused silica heat exchanger depends on the development of successful pore sealing techniques, it was felt that the casting method itself would present sufficient difficulty to warrant early study.

A split wooden master mold was machined to the shell configuration selected for fabrication. The master was well sealed with lacquer and used to cast plaster negative molds. Little difficulty was encountered in casting shells from these molds.

Methods for casting single tubes inside the heat exchanger shell were next investigated. Studies were carried out using plastic cores, plaster cores, cardboard cores, and a variety of other materials to define the inside tube diameter. None of these methods met with success. Finally two stage casting was investigated. First, a tube was shell cast in a plaster mold until the desired wall thickness was obtained. The cast tube was then removed from the mold, partially dried, and mounted through the center of the mold for the exchanger shell. The cast tube was sufficiently dry to cast to the shell and form a firm bond.

Consideration was made of several proposed methods of attaching the cast fused silica heat exchangers to pipe lines. From the standpoint of ease of fabrication and versatility, a joint design was selected which was essentially
identical to that used with Pyrex pipe. Tapered ends were cast on the inlets and outlets of the heat exchangers. These tapered ends were shaped to accept the standard Corning molded asbestos inserts and aluminum flanges, used with Pyrex pipe. With these flanges, connections could be made to standard flanged steel, plastic, or Pyrex pipe. A sectioned exchanger is shown in Figure 28.

A few tests were made in which water was passed through the tube of the exchanger and heated with low pressure steam in the shell. The highest water flow rate used did not exceed laminar flow conditions, giving a Reynolds number of only 1100. Under these flow conditions, the calculated overall heat transfer coefficient was 40 BTU/hr ft² °F.

H. Irradiation Program

Under ordinary conditions, slip cast fused silica is known to have many properties desirable for use in nuclear systems. How these properties may change when the silica is subjected to in-pile irradiation will be investigated in the Westinghouse Testing Reactor. The rate of transformation of any crystalline silica to the amorphous state and the accompanying changes in other properties will be determined as a function of the fast neutron dosage.

1. Test Facility

To carry out this study, the Westinghouse Testing Reactor was chosen because of its desirable high neutron flux, its accessibility, and the fact that initial estimates indicated that samples could be introduced into the reactor at such a time that results would be available for this report. Unavoidable delays in the reactor startup cycle, however, have made this impossible. Design and approval of the experiment have been completed.

For the experiments to be conducted, one of the central experimental capsules was contracted. The fast neutron flux at the centerline in this region should be approximately $5 \times 10^{14}$ nev with the reactor operating at 20 megawatts.
A. SECTIONED

B. PARTIALLY SECTIONED AND WITH FITTINGS

Figure 28. Slip Cast Fused Silica Heat Exchanger.
2. Experimental Procedure.--

Test bars, 0.31 inches in diameter, were cast from the standard slip. The bars had small holes cast in one end to permit insertion of differential thermal analysis (DTA) thermocouples. Each bar can be subjected to post-irradiation modulus of rupture determination, x-ray analysis for ordered cristobalite content, surface area measurement, and DTA to determine stored energy content. Bars with varying initial cristobalite content will be subjected to irradiation.

The test bars will be encapsulated in 6061 aluminum tubing as illustrated in Figure 29. Six of these groups of three tubes will be put into the reactor capsule basket, separated by discs of 1/4-inch thick pure aluminum. This entire assembly will then be deposited into the reactor capsule for twenty-five days of irradiation, giving predicted fast neutron dosages of from 2 to $7 \times 10^{20}$ nvt. Following irradiation, the samples will be taken from the reactor and removed from the capsules in the WTR Hot Cell Facility. At the time of removal, microscopic and other indicated examinations will be performed. At the same time, the aluminum discs placed between the sample holders will be measured using $4\pi$ gamma counting, with energy discrimination, to permit calculation of the aluminum activation. This activation results from the $\text{Al}^{27} (n,p) \text{Mg}^{27}$ reaction, with a threshold energy of 4.6 mev, and the $\text{Al}^{27} (n,\alpha) \text{Na}^{24}$ reaction, 8.1 mev$^3$. Such calculations would yield an estimate of the neutron doses, above the energy levels indicated previously, actually received by the silica samples.

Following this treatment, the samples will be returned to Georgia Tech for post-irradiation examination.

Figure 29. Containment Capsule for Irradiation of Fused Silica.
IV. DISCUSSION

The initial studies of the tensile strength and modulus of rupture of the fused silica as related to firing conditions gave strengthening curves whose shapes were typical for a variety of hardening processes. A distinct similarity was observed to the hardening curves obtained during precipitation hardening of metals. In the case of metals, this hardening results from the lattice distortion and slip blockage resulting from the precipitation of a second metal phase. The initial stage of this precipitation results in an increase in strength due to the nucleation and growth of the second phase. Further heating eventually causes a decrease in strength by agglomeration of the precipitated particles of the second phase.

The shape of the strength curves for silica, as well as careful consideration of the possible sources of particle bonding, would indicate a process similar in many respects to the precipitation hardening of metals. Since a definite trend, although not a quantitative correlation, was noted in the strength increase with cristobalite increase during firing, it appears safe to say that cristobalite nucleation and growth accounts for strengthening.

Cristobalite occurrence is known to occur preferentially at the surface of a fused silica particle. Crystallization occurs in contact with an already crystallized surface, and there is a tendency, in many cases, for the crystallizing phase to present an orientation of the crystallized phase. In the case of slip cast fused silica, crystallization would nucleate and grow along the faces of the particles inward. Once the surface of a particle presents an ordered crystal lattice orientation, contacts. In the contacting
particles, cristobalite formation would then appear quite likely to follow the lattice orientation already established at the particle juncture, with inter-particle crystal growth resulting. This linkage by cross-particle cristobalite growth is thought to account for the strengthening of slip cast fused silica associated with firing.

Longer firing would cause the cristobalite to grow further. As the cristobalite crystallite size increases, greater thermal stresses would arise in the particle bonds, during post-firing cooling, as a result of the cristobalite inversion. Eventually, as the cristobalite crystallite size continues to increase, the weakening effect resulting from thermal stressing and microcracking will overcome the strengthening effect of the increased particle bonding, and the fired strength of the silica will decrease. Such a mechanism would account for the peaks noted in the strength curves of Figures 4, 7, and 8.

Strengthening of the silica during firing would thus appear to occur through crystallite nucleation and growth, as is the case with precipitation hardening metals. The decrease in strength on longer heating, however, would seem to result from increased bond fracture through thermal shock rather than from the particle agglomeration noted in the precipitation hardening of metals. Although concrete results have not yet been obtained, electron microscopy and selected area electron diffraction should serve to evaluate this reasoning.

The tracer permeation studies initially made followed the predicted behavior. Direct correlation of the permeation coefficients with porosity is expected to result from more complete investigations.

The results of the initial x-ray studies have proven to be at variance with the results of Verduch.\textsuperscript{4} The disagreement of the rate curves determined,\textsuperscript{4} A.G. Verduch, "Kinetics of Cristobalite Formation from Silicic Acid", J. Am. Ceram. Soc. 41, 427-432 (November 1958).
using the x-ray techniques developed, with those of Verduch is not surprising in view of the great difference in particle size of the two materials studied. Since the crystallization process is a surface phenomenon, the rate of crystallization would be expected to depend on specific surface area and therefore on particle size. This is shown by a comparison of the surface and bulk cristobalite curves of Figures 24 and 25. During the slip casting process, the flow of water to the mold pulls the finer silica particles to the casting surface through the pores between the larger particles. A much faster rate of crystallization would thus be expected at the cast sample surface where the fine particles accumulate, than in the bulk of the sample. This expected behavior was noted in the curves obtained.
V. PERSONNEL

The work discussed in this report was conducted in the Ceramics Branch, Mr. J. D. Walton, Head. The project was directed by Dr. J. D. Fleming with Mr. J. W. Johnson acting as assistant project director. Contributing personnel, with the approximate times devoted to the project were:

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MATERIALS FOR
HIGH TEMPERATURE NUCLEAR ENGINEERING APPLICATIONS

By
J. D. FLEMING AND J. W. JOHNSON

CONTRACT NO. AT-(40-1)-2483
U. S. ATOMIC ENERGY COMMISSION

15 AUGUST 1959 to 15 AUGUST 1960

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

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FOREWORD

The investigation reported in this document was performed by the Engineering Experiment Station of the Georgia Institute of Technology under U. S. Atomic Energy Commission Contract No. AT-(40-1)-2483. The work was sponsored by the Division of Reactor Development, Fuels and Materials Development Branch, Mr. Julius M. Simmons, Chief. The contract was administered by the Oak Ridge Operations Office, Reactor Division, Dr. David F. Cope, Director.

This report covers the period from 15 August 1959 to 15 August 1960.
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I. INTRODUCTION

The excellent thermal shock resistance and indications of good radiation resistance of fused silica have recommended it for consideration for use in high temperature radiation fields. With the development at Georgia Tech of techniques for economical fabrication of large and complex silica shapes by slip casting, major objections to this material, on the basis of cost and fabrication difficulty, have been overcome.

Although the art of fused silica is well developed, many gaps are still existent in its science. Insufficient data are available for the intelligent evaluation of fused silica as a reactor material. One object of Project B-153 is the development of sufficiently reliable data for, and basic understanding of, fused silica to permit this evaluation.

Fused silica is unique among slip casting materials in the small amount of drying and firing shrinkage associated with raising its density above ninety per cent of theoretical. If other materials could be caused to display a similarly low shrinkage, much better advantage could be taken of slip casting as a fabrication technique. A second object of Project B-153 is the optimization of slip casting ceramics, particularly uranium dioxide, through a comparison of silica with different materials and a basic study of the mechanism of slip casting.

With the growing interest in nuclear propulsion, desired operating temperatures for reactors are steadily increasing. As the operating temperature increases, much higher fabrication temperatures become necessary and forming costs increase rapidly. One method of decreasing forming costs would be using internally generated heat to sinter the desired refractory products of exothermic reactions. Project B-153 is also intended to explore the applicability of such an approach to the generation of practical fuel materials.
II. SUMMARY

Investigations of the properties of slip cast fused silica were furthered. The slip used had a particle size distribution of 94 per cent less than 44 microns and 13 per cent less than 1 micron. A statistical study was carried out to evaluate the relative importance of the different slip casting variables. The most important variables were the nature of the slip and the firing conditions, as was expected. Proof was obtained of the lack of importance of operator and plaster differences as long as standard practices in the field were followed.

Analyses were made of the surface contamination of the silica resulting from the mold plaster and the Keltex mold release normally used. Contamination was minimized by removal of the Keltex prior to firing or by using a graphite mold release developed in this study.

Vibration of the silica slip during casting was investigated as a means of promoting uniformity in fired strengths. Vibration was found to increase the reproducibility of fired strength by a factor of about two but to result in a substantial decrease in the level of strength.

Methods of heat treating the slip cast fused silica were explored in an attempt to increase the strength of fired silica bodies. None proved successful.

Tensile strengths of the silica were determined at elevated temperatures using both conventional methods and a ring tensile tester. Although evaluation of the ring testing method was not completed, the initial results compared well with those of conventional tests and were somewhat more reproducible. The tensile strength of the silica varied from approximately 3,000 psi at room temperature to approximately 8,000 psi at 2000°F.

Mathematical analysis of the tracer gas permeation measurement system was completed. The simple approach proposed in previous work was proved valid. Studies were begun to decrease the permeability of the porous silica by various
sealing techniques.

Design studies were begun for the construction of an electron microscope hot stage for the investigation of the bonding method of slip cast fused silica and the mechanics of devitrification of fused silica. Development of a temperature monitor for the hot stage was begun.

Devitrification studies of slip cast fused silica were continued using a high temperature x-ray diffractometer. Difficulties with platinum evaporation from the heating elements prompted development of a new furnace.

Preferred orientation of the devitrification products in fused silica was investigated. An orientation of the (101) planes of cristobalite parallel to the sample surface was found.

Fused silica was irradiated to a total fast dose of $1.5 \times 10^{20}$ nvt in the Westinghouse Testing Reactor. The cristobalite in the fired samples was reconverted almost completely to amorphous silica under the irradiation. A statistical study of the irradiated bars failed to indicate any influence of the irradiation on the strength of slip cast fused silica.

An experiment was designed to allow irradiation of fused silica at high temperatures produced by gamma heating. Mathematical analysis of the experiment predicted that centerline temperatures of approximately $2500^\circ F$ will be produced in the silica.

A comparative study of the slip casting behavior of several different refractory materials was begun. An alumina slip was developed which yielded bars with a fired modulus of rupture in excess of 20,000 psi.

A system was constructed for motion photomicrography of slip casting. Studies of the slip casting behavior of silica and alumina were initiated.

Investigations were begun of the formation of refractory fuel mixtures by self-sintering exothermic reactions.
III. EXPERIMENTAL WORK

A. FUSED SILICA

1. Slip Evaluation

Since the slip used in the previous year's work was exhausted, a new supply was obtained from Glasrock Products, Inc. The particle size distribution of the new slip and the old slip are compared in Figure 1.

In order to establish optimum firing conditions for the new slip, a firing profile was run. 0.75-inch diameter transverse test bars were cast in plaster molds according to standard practice, dried, and fired at temperatures of 2000, 2100, 2200, and 2300°F for times ranging from 1/2 hour to 16 hours. Following firing, the bars were transverse tested in three point loading. The results of this study are shown in Figure 2. As with the previous slip, a firing temperature of 2200°F was found to be an optimum for high strength, easy firing control, and reasonable firing cycle time.

2. Analysis of Fabrication Variables

Past difficulties with obtaining reproducible strengths in the slip cast fused silica prompted a study of the relative influence of the fabrication variables. The variables which would be expected to influence the strength of the silica were critically surveyed. From this survey, the three variables of mold condition, type of slip, and firing conditions, both temperature and time, were selected for detailed investigation.

0.75-inch transverse bars were cast from silica slips of two particle size distributions as shown in Figure 3. The bars were dried overnight at 280°F. Following drying, groups of the bars were fired in a tube furnace, an Inconel box in a bottom loading furnace, and a cast silica box in a bottom loading furnace.
Figure 1. Comparison of Particle Size Distributions of Standard Slips.
Figure 2. Firing Profile for New Silica Slip.
Figure 3. Particle Size Distributions of Slips Used in Fabrication Variable Study.
The bars were fired at $2200^\circ F$ for four hours. Following firing, three point transverse tests were made.

A standard statistical analysis was carried out using the modulus of rupture data. Calculations were made of the mean square due to each individual variable, all possible combinations of the three variables and of the error variance applying to the series of tests. The influence of each variable and each combination of variables on the fired strength was evaluated by comparing the mean squares with the error variance. A summary of the analysis of variance is given in Table I.

**TABLE I**

ANALYSIS OF VARIANCE FOR FABRICATION TESTS

<table>
<thead>
<tr>
<th>Source of Estimate</th>
<th>Sum of Squares</th>
<th>Degrees of Freedom</th>
<th>Mean Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Firing Method</td>
<td>5,104,839</td>
<td>2</td>
<td>2,552,420</td>
</tr>
<tr>
<td>Slip</td>
<td>3,174,337</td>
<td>1</td>
<td>3,174,337</td>
</tr>
<tr>
<td>Mold</td>
<td>390,637</td>
<td>1</td>
<td>390,637</td>
</tr>
<tr>
<td>Error</td>
<td>7,343,055</td>
<td>32</td>
<td>229,470</td>
</tr>
<tr>
<td>Total</td>
<td>16,012,868</td>
<td>36</td>
<td></td>
</tr>
</tbody>
</table>

The variance was noticed to differ from class to class, leading to a loss of efficiency in the estimation of effects and a distortion of the level of significance of comparisons. An examination of the data, however, shows that the mean square of the mold variable represents no real statistical level of significance while both the firing method and the nature of the slip show significance at the 0.1 per cent level. Since significance at the 5 per cent level is generally considered adequate for statistical reality, the lack of homogeneity among the classes should not negate the qualitative implications of the study.
The variance and standard deviation for the different firing methods and different slips are given in Table II. F ratio tests were made to compare the different conditions. The variance of modulus of rupture differs significantly for bars from the two slips fired in the inconel box but the variance does not differ significantly for firing in the tube furnace and the silica box. The general indications are thus that the variances associated with the firing methods are similar and independent of the slip. This would imply a direct quantitative association of firing method with lack of reproducibility in strength rather than a complex interplay of slip variations and non-uniform firing method. The relatively low variance of firing in the silica box would be expected because of the slower heating and the shorter dwell time in the temperature range critical for cristobalite formation.

### Table II

<table>
<thead>
<tr>
<th>Firing Method</th>
<th>Slip</th>
<th>Variance</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inconel Box</td>
<td>1</td>
<td>762,650</td>
<td>870</td>
</tr>
<tr>
<td>Inconel Box</td>
<td>2</td>
<td>1,452,834</td>
<td>1,210</td>
</tr>
<tr>
<td>Tube Furnace</td>
<td>1</td>
<td>1,764,815</td>
<td>1,330</td>
</tr>
<tr>
<td>Tube Furnace</td>
<td>2</td>
<td>1,766,056</td>
<td>1,330</td>
</tr>
<tr>
<td>Silica Box</td>
<td>1</td>
<td>844,223</td>
<td>920</td>
</tr>
<tr>
<td>Silica Box</td>
<td>2</td>
<td>707,222</td>
<td>840</td>
</tr>
</tbody>
</table>

The preceding conclusions must be emphasized to apply only to the reproducibility of strengths of bars cast from a particular slip and not to any equivalence of fired strengths of different slips. This will obviously depend
on the similarity of particle size distributions of the different slips. Within limits, the strength will increase with an increasing amount of submicron material. In this study, for instance, the submicron content of slip No. 2 was 11 per cent as compared with 6 per cent for slip No. 1. The strength data, tabulated in Table III, show slip No. 2 to be uniformly stronger than No. 1.

**TABLE III**

**STRENGTHS OF BARS CAST FROM SLIPS NO. 1 AND 2**

<table>
<thead>
<tr>
<th>Firing Method</th>
<th>Slip No.</th>
<th>Transverse Strength (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inconel Box</td>
<td>1</td>
<td>2550</td>
</tr>
<tr>
<td>Inconel Box</td>
<td>2</td>
<td>2950</td>
</tr>
<tr>
<td>Tube Furnace</td>
<td>1</td>
<td>3190</td>
</tr>
<tr>
<td>Tube Furnace</td>
<td>2</td>
<td>4040</td>
</tr>
<tr>
<td>Silica Box</td>
<td>1</td>
<td>3190</td>
</tr>
<tr>
<td>Silica Box</td>
<td>2</td>
<td>3720</td>
</tr>
</tbody>
</table>

3. Influence of Type of Plaster

One of the important variables in slip casting would certainly be the plaster used in molding. In order to achieve optimization of the plaster handling, a systematic study was made of three good mold plasters, U. S. Gypsum Pottery Plaster No. 1 and Puritan Plaster, and Bestwall No. K-55. Since all plasters were used in the range previously determined to be best for each type, the study was of an optimum nature, not intended to compare the plasters across the entire composition range.

The 0.75-inch transverse bar molds were cast from each plaster at each composition in the optimum range. The molds were conditioned, by soaking in water and drying, and two castings were made in each. The cast silica bars
were randomly fired in nine groups of 40 bars each for four hours at 2200°F. The transverse strengths of the bars are shown in Table IV.

### TABLE IV

**TRANSVERSE STRENGTHS OF SILICA CAST IN DIFFERENT PLASTERS**

<table>
<thead>
<tr>
<th>Composition (Parts water/100 parts plaster)</th>
<th>Transverse Strength (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Gypsum No. 1</td>
<td>4900</td>
</tr>
<tr>
<td>Gypsum Puritan</td>
<td>5180</td>
</tr>
<tr>
<td>Bestwall K-55</td>
<td>4670</td>
</tr>
<tr>
<td>72</td>
<td></td>
</tr>
<tr>
<td>Gypsum No. 1</td>
<td>4950</td>
</tr>
<tr>
<td>Gypsum Puritan</td>
<td>5030</td>
</tr>
<tr>
<td>Bestwall K-55</td>
<td>5090</td>
</tr>
<tr>
<td>64</td>
<td></td>
</tr>
<tr>
<td>Gypsum No. 1</td>
<td>4940</td>
</tr>
<tr>
<td>Gypsum Puritan</td>
<td>4960</td>
</tr>
<tr>
<td>Bestwall K-55</td>
<td>4630</td>
</tr>
</tbody>
</table>

Examination of the data showed that, although the Puritan plaster seemed slightly superior to the others, there was no statistically significant difference in the strengths of the silica cast in the different plasters. Tests on the plaster strength and speed of casting showed the Puritan to be slightly weaker and slightly faster in casting than the other types. Since workers with the plaster preferred the handling qualities of the Puritan plaster and since Puritan appeared as good as or better than the other plasters, it was selected for standard use.

For general use, a composition of 80 parts of water to 100 parts of plaster was employed. The plaster was sifted into water with a small flour sifter and allowed to slake for five minutes. After slaking, the plaster was mixed at about 1500 RPM in a MixMore No. DS-14 mixer for two minutes. Following mixing, the plaster was poured and allowed to set for 30 minutes. The molds were dried.
Methods were developed through which analyses could be made of the surface composition of the slip cast fused silica. These techniques were applied to a determination of the surface contamination resulting from leaching of the plaster during casting.

A set of Spex Industries trace element G standards were obtained for a sensitivity evaluation of the X-ray fluorescence system. These standards contained 0.1, 0.01, 0.001, and 0.0001 per cent of 42 elements in a carbon matrix. The carbon matrix permitted good estimation of the quantitative accuracy which could be expected from the light silica base material. Four successive readings were made on the K spectral lines of eight of the elements contained in the standards. Following evaluation of the instrument sensitivity from these scans, tests were made of silica slip cast in various plasters. The only element seen to vary significantly among the samples was calcium. On unfired samples the surface calcium content could be reduced several orders of magnitude simply by stripping off the Keltex film which usually adhered to the surfaces on removal from the mold. If the Keltex were left in place during firing, however, the calcium was fixed and could not be removed by scraping. Typical surface analyses of samples fired with the Keltex film in place are given in Table V.

<table>
<thead>
<tr>
<th>Plaster</th>
<th>Fe (%)</th>
<th>Mo (%)</th>
<th>Zr (%)</th>
<th>Cu (%)</th>
<th>Ca (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bestwall K-55</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.0003</td>
<td>0.02</td>
</tr>
<tr>
<td>U. S. Gypsum Puritan</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.0003</td>
<td>0.03</td>
</tr>
<tr>
<td>U. S. Gypsum No. 1</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.0003</td>
<td>0.04</td>
</tr>
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</table>
Keltex releasing agent had been used in all previous casting work. Although Keltex is a most effective mold release agent, its use introduces certain difficulties into slip casting of silica. Since Keltex is a sodium alginate, failure to remove it from the cast silica surface prior to firing will result in the permeation of sodium into the silica. The presence of sodium in silica results in an increased rate of devitrification. The Keltex also appears to trap calcium from the plaster mold and increase the calcium content on the surface of the silica. This would not only increase the rate of devitrification but would represent undesirable surface contaminants from a nuclear standpoint. The contaminating effects of using Keltex can be largely eliminated, however, by stripping the film prior to firing.

Graphite suspensions in organic vehicles have been applied to slip casting of ceramics (1). Efforts were made to form a suspension of graphite which would be compatible with the silica slip in order to give better releasing properties as well as to decrease surface contamination of the silica. Dixon's No. 635 flake and Dixon's Micro Fyne graphite were dry milled and attempts were made to suspend the milled materials in a variety of polar media. Although quasi-stable suspensions were produced, none was completely satisfactory.

In order to obtain better suspensions, the two types of graphite were wet milled in methanol, ethanol and isopropanol and in water with triethanolamine, oleic acid, and gum arabic as dispersants. Of the mixtures tried, the gum arabic proved the most successful. Optimization studies showed that the best stock slurry was produced by milling a 1120 gm charge of 35.6 per cent Dixon's Micro Fyne graphite, 62.3 per cent water, and 2.1 per cent gum arabic.

---

1 Private communication with R.E. Cowan and S. D. Stoddard, Los Alamos Scientific Laboratory, CMB Division.
A one gallon mill was used at 60 rpm for 120 hours with a 4000 gm ball charge. The working suspension was produced by dispersing the stock slurry in water to form a one per cent mixture. The resulting mixture was quite stable and gave excellent mold release coatings when poured into and immediately emptied from the mold. The graphite coating adhered to the mold so that recoating was necessary only after four to five castings.

A series of transverse test bars was cast using Keltex releasing agent and the graphite suspension. The bars were fired randomly in order to compare the strengths resulting from the use of Keltex and from graphite. The results of this test, in which the Keltex was stripped from the casting prior to firing, are given in Table VI.

The results of this test indicated generally higher strengths from the graphite mold release than from the Keltex. Although the reason for this behavior is not yet clearly understood, it is almost certainly due to either less contamination, hence less local devitrification, by the graphite or faster and more uniform casting.

**TABLE VI**

**COMPARISON OF TRANSVERSE STRENGTH WITH KELTEX AND WITH GRAPHITE**

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>2000</th>
<th>2100</th>
<th>2200</th>
<th>2300</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 hrs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Keltex Transverse Strength (psi)</td>
<td>4400</td>
<td>5490</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite Transverse Strength (psi)</td>
<td>3000</td>
<td>3560</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Keltex Transverse Strength (psi)</td>
<td>1240</td>
<td>940</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite Transverse Strength (psi)</td>
<td>1580</td>
<td>1630</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 hrs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Keltex Transverse Strength (psi)</td>
<td>2790</td>
<td>2820</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite Transverse Strength (psi)</td>
<td>1580</td>
<td>1630</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Continued
TABLE VI (Continued)

COMPARISON OF TRANSVERSE STRENGTH WITH KELTEX AND WITH GRAPHITE

<table>
<thead>
<tr>
<th>Temperature (^{\circ}F)</th>
<th>2000</th>
<th>2100</th>
<th>2200</th>
<th>2300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (hr)</td>
<td>Keltex</td>
<td>Graphite</td>
<td>Keltex</td>
<td>Graphite</td>
</tr>
<tr>
<td>4</td>
<td>1730</td>
<td>1660</td>
<td>3980</td>
<td>4100</td>
</tr>
<tr>
<td>8</td>
<td>2900</td>
<td>2610</td>
<td>4880</td>
<td>5050</td>
</tr>
<tr>
<td>16</td>
<td>3900</td>
<td>3693</td>
<td>4160</td>
<td>5900</td>
</tr>
</tbody>
</table>

5. Influence of Vibration During Casting

Since sedimentation of the larger particles is invariably a problem with slip casting, any process which would inhibit settling should give more uniform castings. Ultrasonic and mechanical vibration would be obvious choices for first trials.

A series of test bars was cast in which half the bars were cast in the normal fashion and half were cast while being vibrated with a Syntron vibrator. The cast bars were fired randomly in a bottom loading furnace and transverse tested. Although the test was not extensive enough to furnish concrete indications of the effects of vibration, two trends were noted. The vibrated bars showed a smaller range of deviation, as is shown in Table VII and were generally weaker. The higher degree of uniformity was to be expected from the homogenizing influence of the vibration. Apparently, however, the vibration decreased the degree of particle packing below the level normally associated with movement of the slip in ordinary casting. A more extensive study was begun to confirm these results.
TABLE VII

COMPARISON OF SILICA SLIP CAST WITH AND WITHOUT VIBRATION

<table>
<thead>
<tr>
<th>Group No.</th>
<th>Casting Method</th>
<th>Avg. Transverse Strength (psi)</th>
<th>Maximum Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Vibrated</td>
<td>3720</td>
<td>19.6</td>
</tr>
<tr>
<td>1</td>
<td>Not Vibrated</td>
<td>3370</td>
<td>49.3</td>
</tr>
<tr>
<td>6</td>
<td>Vibrated</td>
<td>1270</td>
<td>11.2</td>
</tr>
<tr>
<td>6</td>
<td>Not Vibrated</td>
<td>1360</td>
<td>11.1</td>
</tr>
<tr>
<td>8</td>
<td>Vibrated</td>
<td>1280</td>
<td>5.78</td>
</tr>
<tr>
<td>8</td>
<td>Not Vibrated</td>
<td>1370</td>
<td>21.6</td>
</tr>
<tr>
<td>10</td>
<td>Vibrated</td>
<td>2840</td>
<td>23.7</td>
</tr>
<tr>
<td>10</td>
<td>Not Vibrated</td>
<td>4130</td>
<td>44.0</td>
</tr>
</tbody>
</table>

6. Notch Sensitivity

In conjunction with design of the various tensile test specimens used, questions arose as to the notch sensitivity of the slip cast fused silica. With a body composed of bonded, irregular, brittle particles, there was a possibility that internal notch effects, resulting from the angular particle shapes, would over-ride macroscopic external notch effects. In order to qualitatively evaluate the effects of external notches, a series of 80 bars was cast using configurations having different notches as shown in Figure 4. The sample size was made such that the area at the restriction was the same in all cases. The results of transverse tests of these bars are given in Table VIII. The data show that a notch sensitivity characteristic of a dense brittle material also applies to the slip cast fused silica.
Figure 4. Slip Cast Fused Silica Notch Effect Samples.
TABLE VIII

TRANSVERSE STRENGTHS OF NOTCHED BARS

<table>
<thead>
<tr>
<th>Bar Configuration</th>
<th>Transverse Strength (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5-in. Straight Bar</td>
<td>2960</td>
</tr>
<tr>
<td>0.5-in. Radius Notch</td>
<td>2150</td>
</tr>
<tr>
<td>0.125-in. Radius Notch</td>
<td>1980</td>
</tr>
<tr>
<td>45° Angle Notch</td>
<td>1730</td>
</tr>
</tbody>
</table>

7. Heat Treatment

Based on observations made during the initial work with the silica, a bonding mechanism was proposed in which the silica particles would be joined by cross-particle cristobalite growth during firing. Due to the β-α cristobalite inversion during cooling, stresses would be expected to arise in the regions of the cristobalite particle junctures. These stresses could result in a decrease in the strength of the fired silica.

An attempt was made to minimize the effects of the cooling stresses by proper heat treatment of the fired silica. A series of 120 0.75-inch transverse test bars was fired at 2200°F for 4 hours. Immediately following the firing, the bars were subjected to various heat treatment shown in Table IX.

TABLE IX

POST-FIRING HEAT TREATMENTS

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Direct quench in still air to room temperature.</td>
</tr>
<tr>
<td>b</td>
<td>Soak 4 hours at 650°F, 4 hours at 450°F, quench to room temperature.</td>
</tr>
<tr>
<td>c</td>
<td>Quench to room temperature, reheat for 4 hours at 400°F, quench to room temperature.</td>
</tr>
</tbody>
</table>

Continued
Following the heat treatment, the bars were transverse tested. The resulting strengths are shown in Table X. From the close correspondence of these values, it is apparent that either the stresses imposed on the silica by direct quenching are of too low an order to show a strength improvement on stress relief or that the cristobalite particle size and distribution are such that particle fracture invariably occurs even on slow cooling. Further studies with a higher cristobalite content would undoubtedly distinguish between these effects.

TABLE X
TRANSVERSE STRENGTHS OF HEAT TREATED SILICA

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Average Transverse Strength (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>4750</td>
</tr>
<tr>
<td>b</td>
<td>4270</td>
</tr>
<tr>
<td>c</td>
<td>4610</td>
</tr>
</tbody>
</table>

Continued
TABLE X (Continued)

TRANSVERSE STRENGTHS OF HEAT TREATED SILICA

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Average Transverse Strength (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>4350</td>
</tr>
<tr>
<td>e</td>
<td>4550</td>
</tr>
<tr>
<td>f</td>
<td>4990</td>
</tr>
<tr>
<td>g</td>
<td>4320</td>
</tr>
<tr>
<td>h</td>
<td>4740</td>
</tr>
</tbody>
</table>

8. Determination of Tensile Strength

Work begun during the last contract year was continued toward satisfactory determination of the room and elevated temperature tensile strength of slip cast fused silica. As a result of the increase in strength of the silica with temperature, heating of the entire test specimen was necessary to avoid cold temperature alloy holding fixtures were used with threaded specimens in the initial work. These specimens were inductively because of the stress concentration effects. Bars were cast in which the threads were rounded and broken at 18 resistance heater to evaluate their usefulness. A number of these samples were used in the threaded areas still predominated.

In an effort to minimize concentration effects, smaller bars of the B configuration, these bars, referred to as D tensile specimens,
were 0.25-inch in diameter at the smallest point and approximately four inches long. D specimens could be used with the threaded specimen holders by means of graphite or Inconel split ring adapters. A D specimen is shown with the ring adapters and threaded holders in Figure 5.

Furnace designs were surveyed to select a suitable heating system for the D specimens. In order to avoid the temperature limitations of conventional resistance heated furnaces, a furnace was built which utilized slip cast fused silica structural components and a mixture of graphite and silicon carbide as a resistance element. The furnace tube was a 1.75-inch diameter, six inch long silica cylinder which was held in a cast silica shell to form an annular space for the resistance mixture. The shell was insulated with silica foam. The annular heating space was filled with a tamped mixture of 50 per cent flake graphite and 50 per cent 320 grit silicon carbide. A drawing of the furnace is shown in Figure 6. Power was fed to the furnace at 30 volts by a step-down transformer controlled by a Variac.

Since fused silica was used for all structural components in the furnace and since loose graphite-silicon carbide powder was used as the heating element, no attempt was necessary to avoid thermal shock through rapid heating. Full line power was applied to the cold furnace and heating was allowed to proceed as rapidly as possible. A power input of approximately 1.5 kva was sufficient to heat the first furnace to 2400°F in two hours. A second furnace, with more insulation, was heated to 2500°F in 30 minutes at a power consumption of 2 kva. The furnaces proved quite stable in operation and gave little trouble.

A series of D specimens was cast and fired at 2200°F for times of 2, 4, and 8 hours. These specimens were tensile tested at room temperature, 1000°F, 1500°F, and 2000°F. Results of these tests were consistent in trend with data obtained from larger specimens but were displaced in magnitude to strengths from 60 to 90 per cent greater than those obtained for the large specimens.
Figure 5. D Tensile Test Specimen and Holder.
Figure 6. Silicon Carbide - Graphite Furnace.
The considerably higher strengths indicated by tests with the D configuration appeared to be primarily due to the greater ease of firing these specimens without warping. The larger specimens used in previous work were so massive that distortion tended to occur during firing as a result of non-uniform heating. Distortion tended to cause misalignment during tensile testing and gave low tensile test strengths. Even with the D tensile specimens, warping remained a problem. Visual examination usually showed that approximately 30 per cent of the D bars in a typical firing would be warped.

In order to overcome the handling and testing problems with conventional procedures, a new system was built based on work at the Armour Research Foundation (1). This system applies compression to a ring perpendicular to its axis, causing tensile fracture to occur in the loading plane. The ring tensile test developed by the Armour Research Foundation offered the best promise of avoiding the difficulties caused by warping. The flat toroidal geometry of the rings proved very resistant to warping and the test itself suffered less from misalignment than conventional tensile tests. Following completion of the ring tester, use of the ordinary D tensile specimens was discontinued and testing of rings was begun.

The system constructed consists of a Hot Rod furnace supported on an I beam superstructure with a bottom loading hydraulic system. The upper compression platen is a silicon carbide plate and the lower compression platen is fused silica. The lower platen is supported on an Inconel cylinder with a quick connect coupling for attachment to the hydraulic pump piston. The Inconel cylinder, lower compression platen, and sample rest in a refractory slide chamber which can be pulled from the furnace for loading when disconnected from the pump piston. The Vickers hydraulic system consists of the pump, 

flow control valve, and a precision regulating valve. The load on the system is recorded by a Minneapolis-Honeywell strip chart recorder whose input source is a Baldwin SR-4 pressure cell tapped into the hydraulic cylinder body. The furnace power is supplied by a Variac and GE transformers with anticipating on-off control furnished by a Wheelco 407 controller.

A diagram of the body of the ring tester is shown in Figure 7. Schematics of the electrical and hydraulic systems are shown in Figure 8 and 9. An overall view of the system is shown in Figure 10.

Fabrication studies were carried out to develop methods for castings rings of fused silica. The principal difficulty encountered in ring casting was fabrication of a suitable core for the definition of the ring inside diameter. Plaster cores were used in the preliminary studies. These cores gave good casting characteristics but were excessively soft and subject to scratching during removal from the casting. For this reason plaster cores were useable only once and were discarded in favor of aluminum, brass, or silica cores, all of which proved satisfactory. Brass cores offered the advantages of economy and good surface finish but the slip cast fused silica gave somewhat better abrasion resistance. Both core materials were used in routine ring casting. The ring mold finally selected was a closed two piece mold having a central passageway for the core and two pouring spouts parallel to the axis of the core. A typical mold and ring are shown in Figure 11.

A series of fused silica rings was slip cast for initial room temperature testing. Following dead weight calibration of the hydraulic system, the rings were tested. A loading rate of approximately 500 pounds per minute was set by means of the variable flow control valve. Clearly defined breaking load peaks were observed on the recorded load charts along with an essentially instantaneous load release upon fracture. Typical load recordings are shown in
Figure 7. Sectioned View of Ring Tensile Tester.
Figure 8. Diagram of Electrical System of Ring Tensile Tester.
Figure 9. Diagram of Hydraulic System of Ring Tensile Tester.
Figure 10. Ring Tensile Tester.
Figure 11. Ring Mold and Specimen.
Figure 12. The fracture patterns in the samples were as expected, with pyramidal fracture planes radiating from the points of loading. A typical fractured sample is shown in Figure 13.

The initial tensile test series gave a room temperature tensile strength of 3,330 psi with a maximum deviation of 14.6 per cent. A similar set of rings was fabricated and forwarded to Armour for testing in their ring testing apparatus. The strength obtained was 3,260 psi with a maximum deviation of 24 per cent. A series of D tensile test bars was fabricated at the same time as the ring specimens and selected samples free of warping were tested in the conventional fashion. These tests gave a room temperature tensile strength of 3,250 psi with a maximum deviation of 37 per cent.

The exceedingly close agreement among the three series of tests was probably fortuitous but was nonetheless promising. In addition, the greater degree of uniformity in the ring tests represented a most useful improvement.

A series of elevated temperature tensile tests was made to check out the system. Runs were made to 2200°F without difficulty. The results of these runs are shown in Figure 14. The high temperature strength of the silica obtained from the ring tests was much higher than that obtained using D specimens. Studies were begun to explain these differences.

9. Sealing Studies

Mathematical verification was completed of the tracer gas technique used for measuring the permeability of slip cast materials. For the purpose of completeness, the entire method is reviewed in the following section.

A permeation system was constructed for the determination of effective diffusivities for krypton flow through porous slip-cast fused silica at room temperature. The system consisted simply of two 2-inch I.D. Pyrex pipe crosses between which the silica sample was clamped. Interface gaskets of
Figure 12. Load Chart from Ring Tensile Tester.
Figure 13. Fractured Ring Tensile Testing Specimen.
Figure 14. Variation in Tensile Strength of Slip Cast Fused Silica with Temperature.
overplasticized polyvinyl chloride were used to form a gas-tight seal between the silica disc and the Pyrex crosses. The upper leg of each cross was fitted with valves to allow the crosses to be emptied by water displacement. A schematic diagram of the system is shown in Figure 15.

In an experiment, a glass ampoule containing about 3 mc of krypton 85 was placed in the hot cross, the closure plates bolted on, and the ampoule crushed by a plunger. The activity in each cross was measured, as a function of time, using conventional Nuclear Chicago counting equipment with Geiger detectors. Because the silica sample was sufficiently thick to attenuate the betas, the Geiger tubes were unable to "see" the activity in the opposite cross. As a result, no correction for changing background was necessary. The characteristics of the counting system and background were the same for both crosses.

The following notations are used in this section:

\[ A = \text{area of porous slab perpendicular to direction of tracer gas flow, sq. ft.} \]
\[ a = \text{tracer gas activity in cross, counts/min.} \]
\[ C = \text{tracer gas concentration, lb. mole/cu.ft.} \]
\[ D = \text{effective diffusivity, sq. ft./hr.} \]
\[ G = \text{net flow rate of tracer gas, lb. mole/hr.} \]
\[ K = \text{constant} \]
\[ L = \text{thickness of porous slab, ft.} \]
\[ n = \text{number of tracer gas molecules in cross} \]
\[ v = \text{volume of cross, cu.ft.} \]
\[ x = \text{distance through porous slab from cold side, ft.} \]

Subscript C = cold side
Subscript H = hot side
Figure 15. Schematic Diagram of Permeation System.
The tracer gas activity in a cross would be proportional to the number of tracer gas molecules in that cross, so that

\[ a = K_1 n \]  \hspace{1cm} (1)\]

Since, in the system used, the counting geometry and counting system characteristics were the same for both crosses, the same proportionality constant, \( K_1 \), would apply to both the hot side and the cold side.

The unsteady state diffusion through the silica follows Equation 2.

\[ \frac{\partial C}{\partial \theta} = D \frac{\partial^2 C}{\partial x^2} \]  \hspace{1cm} (2)\]

The boundary conditions applying to this problem are:

a. \( C(0, 0) = 0 \)

b. \( C(L, 0) = K_1 \)

c. \( C(0, \theta) = f_1(\theta) \)

d. \( C(L, \theta) = f_2(\theta) \)

Consideration of Equation 2, under the stated boundary conditions, shows that it is not amenable to simple solution. Solution of even a simplified case similar to these conditions (1) leads to error function of complex argument which have not been tabulated. Consideration of a much less complex problem will indicate that solution of the preceding problem is unnecessary.

Consider a plane slab through which a gas is diffusing from \( x = L \) to \( x = 0 \). For an isotropic solid, this diffusion is represented by Equation 2. Prior to \( \theta = 0 \), the concentration through the solid is a linear function of \( x \). At all times the concentration at \( x = 0 \) is constant. At \( \theta = 0 \), the

---


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concentration at \( x = L \) is suddenly changed from a constant value \( K' \), to a new constant value \( K_2' \).

e. \( C(L, \theta) = K_2' \)

f. \( C(x, 0) = K_3' x \)

g. \( C(0, \theta) = K_4' \)

Converting Equation 2 and boundary conditions e, f, and g to activity, rather than concentration, using Equation 1, yields

\[
\frac{\partial a}{\partial \theta} = D \frac{\partial^2 a}{\partial x^2} \tag{3}
\]

and

h. \( a(L, \theta) = K_2 \)

i. \( a(x, 0) = K_3 x \)

j. \( a(0, \theta) = K_4 \)

Assuming that the activity may be separated into two terms, \( a_\| \) representing the steady state activity at infinite time, and \( a_{\perp\perp} \) representing the deviation from steady state at any time and position,

\[
a_\| = \varphi(x) \]
\[
a_{\perp\perp} = \varphi(x, \theta) \]

If

\[
a = a_\| + a_{\perp\perp} \tag{4}
\]

then

\[
\frac{\partial a_\|}{\partial \theta} = D \frac{\partial^2 a_\|}{\partial x^2} \tag{5}
\]
and

\[ \frac{\partial a_{II}}{\partial \theta} = D \frac{\partial^2 a_{II}}{\partial x^2} \quad (6) \]

Since \( a_I \) is the steady state activity, the solution of Equation 5 is obviously

\[ a_I = K_4 + \frac{(K_2 - K_4)x}{L} \quad (7) \]

The solution of Equation 6 is (1)

\[ a_{II} = \int_0^\infty b_n \sin \frac{n\pi x}{L} e^{-\frac{Dn^2 \pi^2 \theta}{L^2}} \quad (8) \]

in which

\[ b_n = \frac{2}{L} \int_0^L (a_{II})_{\theta=0} \sin \frac{n\pi x}{L} dx \quad (9) \]

From boundary condition 1 and Equation 4,

\[ (a_{II})_{\theta=0} = K_3x - (a_I)_{\theta=0} \]

and, since \( a_I \) is independent of time,

\[ (a_{II})_{\theta=0} = K_3x - K_4 - \left(\frac{K_2 - K_4}{\Omega}\right) (-1)^{n-1} \quad (10) \]

Integration of Equation 9 following substitution of Equation 10 yields

\[ b_n = \frac{2K_3}{\Omega} (-1)^{n-1} + \frac{2K_4}{\Omega} \left(\frac{-1}{(n-1)-1}\right) - \frac{2(K_2 - K_4)}{\Omega} (-1)^{n-1} \quad (11) \]

\[ \text{The convergence and validity of this solution is discussed by Carslaw and Jaeger.} \]
And, from Equations 4, 7, and 8, the general solution for Equation 3 is, under boundary conditions h, i, and j,

\[ a = K_4 + \frac{(K_2 - K_4)x}{L} + \sum_{n=1}^{\infty} b_n \sin \frac{n\pi x}{L} e^{-\frac{Dn^2\pi^2 t}{L^2}} \quad \text{(12)} \]

For short periods of time, Equation 8 converges slowly. To indicate the response of the diffusion system, \( a_{\text{II}} \), the deviation at any time from the activity distribution at \( \theta = \infty \), was calculated by programming Equation 8 for IBM-650 computation to within approximately 1% of the true analytical value. For a 0.25-in. thick silica slab, used in most of the tests, with a representative effective diffusivity of \( 10^{-2} \) sq. ft./hr., Figure 16 shows \( a_{\text{II}} \) for an instantaneous change in hot side activity from 4000 counts/min. to 3900 counts/min. and a constant cold side activity of 0 counts/min.

Figure 16 shows that the concentration gradient through the slab would essentially reach equilibrium in approximately one minute, following the instantaneous hot side activity decrease of 100 counts/min. Figure 17, which shows the change in hot side activity with time in a typical run, indicates that the maximum rate of hot side activity change, occurring during the first hour of operation, is approximately 300 counts/min./hr. The concentration gradient is thus seen to approach linearity at a rate which greatly exceeds the rate of hot side activity change. Under these circumstances, in the system used, the concentration should be very nearly a linear function of position at all times and the system should be adequately represented by the steady state diffusion equation.

\[ G = -DA \frac{dC}{dx} \quad \text{(13)} \]

which, for a plane slab, yields the integral equation

\[ G = \frac{DA}{L} (C_H - C_C) \quad \text{(14)} \]
Figure 16. Activity Deviation from Steady State as a Function of Position.
Since

\[ G = \frac{dn_c}{d\theta} \]  \hspace{1cm} (15)

Equation 12 may also be written

\[ \frac{dn_c}{d\theta} = \frac{DA}{L} (C_H - C_c) \]  \hspace{1cm} (16)

or since

\[ C = \frac{n}{v}, \]

\[ \frac{dn_c}{d\theta} = \frac{DA}{LV} (n_H - n_c) \]  \hspace{1cm} (17)

Substituting Equation 1 in Equation 17 gives

\[ \frac{da_c}{d\theta} = \frac{DA}{LV} (a_H - a_c) \]  \hspace{1cm} (18)

If the diffusion process actually follows a steady state behavior and if the solid being permeated is actually isotropic, Equation 18 indicates that a plot of the slope of the curve of cold side activity vs. time, as a function of the difference in hot and cold side activities, should yield a straight line passing through the origin. The slope, DA/LV, of this line would permit calculation of the effective diffusivity.

Two advantages accompany this method of treating the data. Equation 18 shows that no correction of the data for background is necessary. The background would cancel in the activity difference term, since systems with similar counting characteristics were used, and would not appear in the term for differential cold side activity change. In addition, no knowledge is required
of the specific activity of the tracer gas or of the exact quantity of tracer gas used. Since Kr-85, with a half life of 10.3 yr., was used as the tracer, no correction for radioactive decay was required.

Figures 17 and 18 show the hot and cold side activities as functions of time for a typical run using a silica disc, 0.25-inch thick, fired at 2200°F for four hours. Graphical differentiation of Figure 18 gave the plot of differential activity change as a function of time shown in Figure 19. Figure 20 illustrates the relationship between this differential activity change and the difference in hot and cold side activities. As Equation 18 predicts, a straight line does result, passing through the origin. For this run, the permeability is given by:

\[
D = \text{slope of Figure } 20 \times \frac{LV}{A}
\]

\[
= 0.102 \text{ hr}^{-1} \left(\frac{0.0208 \text{ ft} \times 0.0266 \text{ ft}^3}{0.00545 \text{ ft}^2}\right)
\]

\[
= 1.04 \times 10^{-2} \text{ ft}^2/\text{hr}
\]

Studies were continued toward the development of a method for decreasing the permeability of the slip cast fused silica. Both permeation by organosilicates and flame glazing were surveyed. While flame glazing, with oxy-acetylene or arc plasma torches, produced a dense, glassy surface, the glazed layer thickness was difficult to control and the surface finish obtainable was quite poor.

In order to establish standard soaking procedures for the work with organosilicates, a series of tests was made to determine the time required for the soaking solutions to gel. Mixtures of water and the organosilicates were made up at different concentrations. The solutions were allowed to gel at room temperature and the gelling time was measured. A mixture of tetraethyl orthosilicate containing 18.0 per cent available silica was found to gel in 16 hours. A mixture of Union Carbide ethyl silicate 40 containing
Figure 17. Hot Side Activity as a Function of Time.
Figure 18. Cold Side Activity as a Function of Time.
Figure 19. Rate of Activity Change as a Function of Time.
Figure 20. Rate of Activity Change as a Function of Activity Driving Force.
18.7 per cent available silica was also found to gel in 16 hours. In view of the close correspondence of these values, 16 hours gelling mixtures were chosen for the initial work.

Preliminary studies were made of techniques for permeating silica with the organosilicates. Systems were constructed to maintain a vacuum on the silica being permeated and a pressure on the permeating solution. Trial runs were made in this system to determine optimum effective soaking times for a comparative study. A series of 0.75-inch diameter test bars was cast and samples were soaked for periods of 1, 2, 4, and 8 hours using the vacuum-pressure combination and vacuum alone. Measurements of the deposited silica retained after firing and the open porosity were made. These measurements showed that the rate of soaking under the vacuum-pressure combination was roughly twice that with vacuum alone. Saturation of a six inch long test bar was possible in two hours using vacuum and pressure.

Fabrication was begun of a series of approximately 500 test bars to be used in determining the influence of organosilicate soaking on transverse strengths. The study was planned in such a manner as to allow statistical analysis of the results. A few bars were given initial soakings in ethyl silicate 40. These initial soaking tests indicated an increase in density of approximately 3.2 per cent in one soaking and a decrease in porosity of approximately 7.5 per cent.

An apparatus was constructed to allow vacuum-pressure soaking of discs suitable for permeability measurement by krypton tracer permeation. Soaking and firing of discs was begun.

10. Investigation of Bonding

Design studies were begun for a heated stage attachment for electron microscopy. Such an attachment would be essential for an investigation of
the crystallization mechanics of amorphous silica and the bonding behavior of slip cast fused silica. Construction was begun of a full-scale mockup of the specimen chamber and associated components of the RCA EMU-2 electron microscope to permit access and prototype design of a resistance heated sample holder. The first trial design of the sample holder is shown in Figure 21.

Methods of measuring the grid temperature were considered. The two most feasible appeared to be using either an electronically switched thermocouple-resistance heater circuit switching at high frequency with low noise components or calibrated radiation pyrometry. In either case the system would be developed using the specimen chamber prototype for testing and calibration. Schematic diagrams of the two proposed temperature monitoring systems are shown in Figure 22.

A vacuum evaporation system was constructed for use in forming thin films for transmission electron microscopy. The system uses a Welch mechanical fore-pump and a Consolidated Vacuum Corporation oil diffusion pump. Consolidated Vacuum thermocouple and cold cathode discharge gages are used for pressure monitoring. The system is fitted with quick connect valves to permit use with other equipment requiring vacuum operation.

A separate power supply rated at 2 kva was constructed for use with the vacuum system for vacuum evaporation of thin films. The power supply is also suitable for heating the optical hot stage used in other phases of the investigation.

In support of direct observation of the cristobalite by electron microscopy, two additional physical methods of analysis were explored. Since an absorption of heat accompanies the $\alpha - \beta$ cristobalite inversion, differential thermal analysis should display a peak at approximately 250°C. This peak would be
Figure 21. Proposed Design of Hot Stage for RCA Electron Microscope.
Figure 22. Methods of Grid Temperature Measurement for Hot Stage.
quantitatively related to the mass of cristobalite present in the sample, but not related to the cristobalite distribution. As a result, DTA was expected to serve as a check for bulk cristobalite analysis provided the test conditions could be adequately controlled.

The thermal expansion, on the other hand, would be expected to be dependent on both the mass and distribution of the cristobalite. An interconnected cristobalite matrix would be somewhat less restricted in movement by the associated amorphous silica than a disconnected series of "point precipitated" cristobalite particles. Correlation of the thermal expansion data with bulk cristobalite contents, as determined by x-ray or DTA, could then yield information on the qualitative nature of the distribution of the crystallized areas, i.e., whether the cristobalite occurred as a continuous network or as discontinuous particles. Quantitative indications would not be anticipated in view of the complexity of the system and the uncertainties in thermal stress analysis. Studies were begun to explore these techniques as applied to slip cast fused silica.

11. Devitrification Studies

The investigation of the rate of devitrification of slip cast fused silica was continued. Silica samples, one by two by 0.20 cm., were cast in plaster molds. The samples were dried but not fired prior to testing. The samples were heated in the high temperature diffractometer (1) and maintained at a constant temperature for eight hours. The progress of the devitrification was followed by scanning the top surface of the sample with copper $K_{\alpha}$ radiation through a 2$\theta$ diffraction angle range of 16.5 to 24.5 degrees. Scan cycles of 12 minutes were employed.

In the operation of the platinum wound resistance furnace, films of
platinum were noticed forming on the sample surface by evaporation of the fila-
ments. Since these films decreased the intensity of the diffracted radiation,
a correction was necessary for the continuously growing platinum film. Scanning
angle ranges were adjusted so that both cristobalite and platinum diffraction
peaks were continuously recorded as devitrification proceeded. Following
testing of the samples at elevated temperatures, diffraction data were collected
at room temperature using a standard specimen holder and a scanning speed of
1°/minute. This information was used to obtain a rough estimate of the extent
of preferred orientation of the deposited platinum and to indicate the nature
and amounts of the devitrification products. Diffraction data were next taken
at a scanning speed of 0.5 degrees per minute over selected angular ranges to
permit determination of the terminal amounts of cristobalite and platinum.

Following the diffraction runs, an x-ray fluorescence study was carried
out in which measurements were made of the intensities of the silicon $K_\alpha$
radiation emitted from the surfaces of each sample. Since the samples were
all essentially pure silica, it was possible to calculate the thickness of
the deposited platinum by attributing differences in the silicon intensities
to absorption of the x-rays by the platinum films. A semilog plot of the
intensity ratio, true to observed, as a function of the platinum peak area
was found to be a straight line, as was expected. By combining the information
from these studies, a correction factor was calculated for correction of the
x-ray data for absorption by the platinum films.

Correction factors were applied to the high temperature devitrification
data to yield rate curves. Typical curves are shown in Figure 23. Two
inconsistencies are evident from these curves. The runs at 1700 and 2300°F
show a decreasing percentage of cristobalite with time for the longer runs
and there is no apparent correlation of rate with temperature. Several
Figure 23. Rate Curves for Devitrification of Fused Silica.
sources of these inconsistencies could easily apply. Irregularities in the sample preparation could lead to the lack of uniformity in the effect of temperature on the devitrification temperature. Both the absence of reasonable temperature influence and the decrease in cristobalite could be explained by erroneous or insensitive platinum film corrections.

Two alternate approaches were taken to improve or eliminate the platinum film correction. The correction could be eliminated, at least at lower temperatures, by the use of resistance heaters made from a material which would show less vaporization than the platinum. A furnace of different design was constructed using Kanthal as the heating element. This furnace and the associated equipment are shown in Figure 24 through 28. Evaluation of the furnace at temperature was begun.

At higher temperatures, no suitable alternate to platinum heaters was found which could operate without essentially complete redesign of the diffractometer. In this case, a refinement of the platinum film correction technique was required. The first attempt was measurement of the film correction by angle-dependent attenuation of the diffraction peaks. Although simple, this method failed to provide sufficient accuracy to warrant its adoption.

In a second study, platinum films were deposited, in thicknesses up to 200 Å, on ultra thin Mylar films. These standards, were placed on silica samples and subjected to x-ray fluorescence. Since the absorption of Mylar was negligible, the attenuation of the emitted radiation could be used for measurement of the platinum film thickness. The films were then placed on silica samples in the x-ray diffractometer and diffraction patterns were taken. Correction factors were then calculated from the difference in intensity of the diffracted beam with and without the platinum film in place and the
Figure 24. Assembly View of Elevated Temperature Diffractometer Attachment.
Figure 25. Elevation Adjustment of Elevated Temperature Diffractometer Attachment.
Figure 26. Cooling System for Elevated Temperature Diffractometer Attachment.
Figure 27. Elevated Temperature Diffractometer Attachment in Operation.
Figure 28. Elevated Temperature Diffraction System in Operation.
measured film thickness. These experimentally determined correction factors should provide accurate platinum corrections.

Consideration was also given to shielding of the sample from the platinum heaters by interposition of fused quartz sheets. Since the quartz would devitrify and cloud during the run, difficulties could be expected from this approach. Its full investigation was deferred pending evaluation of the other approaches.

Work was begun to investigate the possibility of preferred orientation of the cristobalite forming during devitrification of fused silica. Samples of fused quartz glass were fired at elevated temperatures to cause devitrification to occur. The samples were placed in a standard specimen holder and subjected to diffraction at selected angles to the sample surface. A definite indication of preferred orientation of the cristobalite (101) planes parallel to the sample surface was given by the marked dependence of the diffracted intensity on angle of incidence. A typical intensity trace is shown in Figure 29.

Studies were undertaken to reproduce the preferred orientation under more carefully controlled conditions. Samples with polished surfaces were fired at closely regulated temperatures. Pole figures will be prepared for these samples.

12. Irradiation Programs

An irradiation program was completed for the study of low temperature neutron damage in silica. Aluminum capsules (1) were fabricated for containment of slip cast fused silica samples.

A series of 0.375-inch bars was cast from the standard slip and fired at 2500°F for 48 hours to insure extensive cristobalite formation. Each bar was

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1 Georgia Institute of Technology, Engineering Experiment Station, Progress Report No. 1, Project B-153, USAEC Contract No. AF-(40-1)-2483, August 1959
Figure 29. X-ray Intensity Trace of Devitrified Silica.
cut into two 1.25-inch and one 0.5-inch lengths. X-ray diffraction runs were made on opposite sides of the longer bars to determine the surface cristobalite content. The shorter length was crushed and analyzed for bulk cristobalite content. Following the x-ray analyses, the 1.25-inch lengths were sealed in the irradiation capsules so that two bars were placed in each axial position in the reactor basket.

Three sets of bars were cast and fired for the study of the influence of neutron damage on the strength of slip cast fused silica. These bars were fired at 2300°F with one set being fired for 1/2 hour, one set for 1 hour, and one set for 2 hours. These three sets bracketed the optimum cristobalite content for 2300°F firing. The bars were subjected to x-ray analysis for cristobalite content, both surface and bulk. Samples were sealed in the irradiation capsules in such arrangement that the bars with higher cristobalite contents were placed in the higher flux positions of the reactor basket and lower cristobalite bars were placed in lower flux positions. Bars fired on each side of the peak strength firing conditions were used so that conclusions could be drawn as to the possibility of bonding by cross-particle displacement of the silica under neutron irradiation.

The sealed irradiation capsules were placed in the Westinghouse Testing Reactor for one cycle. Following irradiation, the sample capsules were removed from the reactor and transferred to a water canal for cooling. After cooling, the samples were removed from the containers and returned for examination. The average fast neutron dose (>0.8 mev) received by the silica was $1.5 \times 10^{20} \text{nvt}$. The samples were unchanged in size or physical appearance by the irradiation.

Considerable trouble was encountered from free surface contamination on the samples. Rough experiments proved that the contamination was external to the silica, probably resulting from handling inside a contaminated hot cell.
The majority of the free contaminant was removed by acid rinsing of the samples. Complete protection against the contaminant was provided by the sealing of the sample with a collodion film. The contaminant was a weak beta emitter but no detailed attempt was made to positively identify it since it did not arise from the silica itself.

The irradiated samples were transverse tested along with a large group of unirradiated samples fabricated at the same time as those which were irradiated. In each case, the average transverse strength was slightly lower, approximately 10 per cent, for the irradiated samples than for the unirradiated samples. Since the number of irradiated samples was small, a careful statistical comparison was made of the transverse strengths of the irradiated and unirradiated samples. In no case did the transverse strengths show a difference greater than about the 75 per cent level of confidence while a 95 per cent confidence level is normally considered minimum for stating statistical significance. As a result, no conclusion may be drawn as to whether the lower strength of the irradiated samples was due to the irradiation or to the small number of samples. As a maximum, at any rate, the irradiation changed the strength no more than 10 per cent.

X-ray diffraction analysis was carried out on the irradiated silica to determine the extent of destruction of the ordered cristobalite structure. In all cases, even in the bars which were initially all cristobalite, little indication of an ordered structure remained.

An experiment was designed to determine the influence of irradiation on the silica at elevated temperatures. The experiment will be a maximum temperature run in which the silica will be insulated in stainless steel capsules and heated by gamma energy only. A rough analysis was made to estimate the temperature which would be attained in the center of the silica.
samples using Alundum insulation. The following assumptions were made:

1. Gamma heat generation in the stainless steel is neglected.
2. The heat transfer is one dimensional.
3. The materials are isotropic.
4. The thermal conductivity does not change with temperature.

Under these assumptions, the central silica sample may be treated by the equation

\[ \frac{k_s}{r} \left( r \frac{d^2 t}{dr^2} + \frac{dt}{dr} \right) + Q_s = 0 \]  

where

- \( k_s \) = thermal conductivity of silica
- \( r \) = radial displacement from sample axis
- \( t \) = temperature
- \( Q_s \) = volumetric heat generation rate.

or

\[ \frac{k_s}{r} \frac{dr}{dr} \left( r \frac{dt}{dr} \right) + Q_s = 0 \]

By separation of variables

\[ \frac{d}{dr} \left( r \frac{dt}{dr} \right) = -\frac{Q_s r}{k_s} \]

Integration gives

\[ r \frac{dt}{dr} = \frac{Q_s r^2}{2k_s} + C_1 \]

\[ t = -\frac{Q_s r^2}{4k_s} + C_1 \ln r + C_2 \]
The boundary conditions which apply are

1. \( \frac{dt}{dr} = 0 \) at \( r = 0 \)
2. \( t = t_s \) at \( r = r_s \)

where

- \( t_s \) = silica surface temperature
- \( r_s \) = radius of silica sample

By the substitution of boundary conditions 1 and 2, Equation 2 reduces to

\[
t = \frac{Q_s}{4k_s} (r_s^2 - r^2) + t_s \tag{3}
\]

which is applicable when

\[
0 \leq r \leq r_s.
\]

For the insulating material, Equation 1 and 2 apply with the proper heat generation rate and thermal conductivity. The first boundary condition arises from the fact that the heat flowing into the insulation must be that generated in the silica.

\[
q_i = Q_s V_s = Q_s (\pi r_s^2 L) \tag{4}
\]

where

- \( q_i \) = heat transfer rate into insulation
- \( Q_s \) = volumetric heat generation rate in silica
- \( V_s \) = volume of silica
- \( L \) = length.

By Fourier's Law

\[
q_i = -k_i A_s \left( \frac{dt}{dr} \right) |_{r_s} \tag{5}
\]

-66-
where

\[ k_1 = \text{thermal conductivity of insulation} \]
\[ A_s = \text{surface area of silica} \]
\[ (\frac{dt}{dr})_{|r_s} = \text{temperature gradient in insulation at } r_s \]

Since

\[ A_s = 2\pi r_s L \]
\[ q_i = -k_1 (2\pi r_s L) \frac{dt}{dr}_{|r_s} \] \hspace{1cm} (6)

Combining Equations 4 and 6,

\[ Q_s r_s = -2k_1 \frac{dt}{dr}_{|r_s} \]

or

\[ \frac{dt}{dr}_{|r_s} = -\frac{Q_s r_s}{2k_1} \] \hspace{1cm} (7)

The boundary conditions are then

1. \[ \frac{dt}{dr} = -\frac{Q_s r_s}{2k_1} \text{ at } r_s \]
2. \[ t = t_i \text{ at } r_i. \]

Substituting the boundary conditions into the proper form of Equation 2 gives

\[ t = \frac{Q_i}{4k_1} (r_i^2 - r^2) + \frac{r_s^2}{2k_1} (Q_s - Q_s) \ln \frac{r}{r_i} + t_i \] \hspace{1cm} (8)
which order analysis shows to be consistent with the system. Equation 8 is applicable when

\[ r_b \leq r \leq r_1 \]

For the stainless steel capsule,

\[ q = \frac{\Delta t}{R} \]

\[ R_{\text{stainless}} = \frac{\ln \frac{r_0}{r}}{2\pi k_c L} \]

where

- \( r_c \) = outside radius of capsule
- \( k_c \) = thermal conductivity of capsule
- \( L \) = axial length of capsule

\[ R_{\text{coolant film}} = \frac{1}{2\pi r_c L h} \]

where

- \( h \) = surface convection coefficient.

Substituting for the series resistances in Equation 10,

\[ q = \frac{t - t_F}{\ln \frac{r_c}{r} + \frac{1}{2\pi k_c L} + \frac{1}{2\pi r_c L h}} \]

where

- \( t_F \) = mean coolant temperature.
The heat transferred will be equal to the sum of the heat generated in the silica and in the insulation.

\[ q = Q_s V_s + Q_1 V_1 \]  \hspace{1cm} (11)

where

- \( Q_s \) = volumetric heat generation rate in silica
- \( V_s \) = volume on silica
- \( Q_1 \) = volumetric heat generation rate in insulation
- \( V_1 \) = volume of insulation

since

\[ V_s = \pi r_s^2 L \]

and

\[ V_1 = \pi (r_1^2 - r_s^2) L, \]

Equation 11 becomes

\[ q = Q_s (\pi r_s^2 L) + Q_1 (\pi [r_1^2 - r_s^2] L) \]

and Equation 10 becomes

\[ Q_s (\pi r_s^2 L) + Q_1 (\pi [r_1^2 - r_s^2] L) = \frac{t_1 - t_F}{\ln \frac{r_c}{r} + \frac{1}{2\pi k_c L} + \frac{1}{2\pi r_c L h}} \]

which reduces to

\[ t = [Q_s r_s^2 + Q_1 (r_1^2 - r_s^2)] \left( \frac{1}{2k_c} \ln \frac{r_c}{r} + \frac{1}{2r_c h} \right) + t_F. \]  \hspace{1cm} (12)
Estimates were made for a typical sample, using HD Alundum insulation, for a 60 megawatt run in a W basket of the WTR. For the hot spot in this case,

\[
Q_s = 28.6 \times 10^5 \frac{\text{BTU}}{\text{ft}^3\text{hr}} \quad \text{(Estimated)}
\]

\[
Q_i = 28.1 \times 10^5 \frac{\text{BTU}}{\text{ft}^3\text{hr}} \quad \text{(Estimated)}
\]

\[
k_c = 9.4 \frac{\text{BTU/hr ft}}{\text{°F}}
\]

\[
k_i = 0.625 \frac{\text{BTU/hr ft}}{\text{°F}}
\]

\[
k_s = 0.4 \frac{\text{BTU/hr ft}}{\text{°F}}
\]

\[
r_c = 0.0688 \text{ ft.}
\]

\[
r_i = 0.0625 \text{ ft.}
\]

\[
r_s = 0.0208 \text{ ft.}
\]

\[
h = 750 \frac{\text{BTU}}{\text{hr ft}^2\text{°F}} \quad \text{(Estimated)}
\]

From Equation 3, 8, and 12

\[
t_i = 299^\circ \text{F}
\]

\[
t_s = 1750^\circ \text{F}
\]

\[
t_o (\text{centerline}) = 252^\circ \text{F}
\]

Figure 30 shows the centerline temperature as a function of axial location for this case.

A 316 stainless steel capsule was machined to fit a W basket in the WTR. The silica samples will be 6-inch long cylindrical bars 0.5-inch in diameter. Six samples will be used.

Trials of three materials were begun to select a suitable insulating core material. Both HD and I Alundum castable appeared to give fairly satisfactory results. Attempts were also begun to cast insulating rings from fused silica. The advantages of using silica would be twofold. First, the silica has a
Figure 30. Variation of Predicted Centerline Temperature in WIR Capsule.
thermal conductivity thirty per cent less than I Alundum and sixty per cent
less than HD Alundum, giving the opportunity of reaching much higher centerline
sample temperatures. Second, if silica rings can be used, they can be tensile
tested using the ring tester described in this report, thereby increasing the
information yield from the experiment to a considerable extent.

Fabrication studies were begun to permit casting holes in the samples and
insulating core to pass thermocouples for temperature monitoring. The thermo-
couples used will be platinum sheathed platinum-platinum 13 per cent rhodium
with alumina insulation.

Figures 31 and 32 show the proposed capsule design.
LIST OF MATERIALS

ITEM NUMBER NEEDED DESCRIPTION AND MATERIAL DIMENSIONS IN INCHES

1 1 1-1/8 In. O.D. x .065 Wall x 240 Inches, Type 304 Stainless Steel Tube
2 6 1/16 In. Diameter Inconel Sheathed Pt. 13% Rh.—Pt. Thermocouples, Sheath Lengths 15, 20, 26, 32, 33 and 39 Inches
3 1 1/16 In. Diameter Platinum Sheathed Pt. 13% Rh.—Pt. Thermocouple, Sheath Length 26 Inches
4 1 1 Inch of 1-7/8 Diameter Type 304 S.S. Rod
5 1 1-1/2 Inch Sch 80 Type 316 S.S. Pipe x 44 In.
6 1 1 Inch of 1-3/4 Diameter Type 304 S.S. Rod
7 1 1-1/2 In. O.D. x 1/2 I.D. x 42-19/32 Fused Silica or Alundum Core
8 7 15/32 x 6 Inches Long Fused Silica Bars

Figure 31. Cross Section of Heated Irradiation Capsule.
Figure 32. Thermocouple Attachments to Heated Irradiation Capsule.
B. SLIP CASTING

Materials were ordered for the development of tungsten and uranium dioxide slips for comparison with fused silica in casting behavior. Since materials were on hand for development of an alumina slip, this work was carried out independently to establish the experimental approach.

Slips were prepared using 60 mesh Norton No. 38 Alundum as the starting material. The grain was 99.5 per cent aluminum oxide with 0.35 per cent of sodium oxide as the most abundant impurity. Table XI describes the slips produced.

**TABLE XI**

**ALUMINA SLIPS STUDIED**

<table>
<thead>
<tr>
<th>Slip No.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Alumina powder produced by dry ball milling 2000 gm. Alundum for 113 hrs. Slip prepared by mixing 333 gm. alumina powder, 66 ml. water 1.3 ml. 36 per cent hydrochloric acid.</td>
</tr>
<tr>
<td>2</td>
<td>Same as No. 1 except 1.1 ml. hydrochloric acid.</td>
</tr>
<tr>
<td>3</td>
<td>Same as No. 1 except 0.8 ml. hydrochloric acid.</td>
</tr>
<tr>
<td>4</td>
<td>Same as No. 1 except 0.7 ml. hydrochloric acid.</td>
</tr>
<tr>
<td>5</td>
<td>891 gm. Alundum milled in 300 ml. water for 48 hrs. pH adjusted from 11.0 to 4.2 with 2.2 ml. 36 per cent hydrochloric acid.</td>
</tr>
<tr>
<td>6</td>
<td>1458 gm. Alundum milled in 230 ml. of 0.7 N hydrochloric acid for 72 hrs.</td>
</tr>
<tr>
<td>7</td>
<td>2000 gm. Alundum milled in 370 ml. of 0.9 N hydrochloric acid for 72 hrs.</td>
</tr>
</tbody>
</table>

All grinding was carried out at 60 RPM in a one gallon porcelain mill using four kg. of 1-1/4-inch alumina balls. Packing of the alumina during dry milling was eliminated by thoroughly drying the charge, the balls, and the ball
mill prior to grinding. The balls and ball mill were saturated with water prior to wet milling to maintain a constant water content in the slip.

For each of the freshly prepared slips, determinations were made of the particle size distribution, pH, specific gravity, and the time required to cast a 0.375-inch diameter test bar. Viscosity measurements were made on the slips prepared from dry milled alumina. The slip pH was again measured following ageing for two days at room temperature.

Test bars, 0.375-inch diameter by four inches, were cast from each freshly prepared slip. Additional test bars were cast from the acid milled slips using low speed vibration to increase the slip fluidity. Following drying of the bars at 230°F for 16 hours, measurements were made of the density, modulus of rupture, and linear shrinkage.

Particle size distributions of the alumina in the various slips are shown in Figure 33. Characteristics of the slips are given in Tables XII through XIV.

**TABLE XII**

CHARACTERISTICS OF SLIPS PREPARED FROM DRY MILLED ALUMINA

<table>
<thead>
<tr>
<th>Slip Properties</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.78</td>
<td>3.90</td>
<td>4.32</td>
<td>4.55</td>
</tr>
<tr>
<td>Apparent Viscosity (cp)</td>
<td>240</td>
<td>194</td>
<td>116</td>
<td>145</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.65</td>
<td>2.65</td>
<td>2.65</td>
<td>2.65</td>
</tr>
<tr>
<td>pH-Aged 2 days</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Casting Properties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Casting Time (Min.)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>Nature of Freshly Cast</td>
<td>Thixotropic</td>
<td>Thixotropic</td>
<td>Thixotropic</td>
<td>Not Thixotropic</td>
</tr>
<tr>
<td>Bars</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
### TABLE XII (Continued)

**CHARACTERISTICS OF SLIPS PREPARED FROM DRY MILL ED ALUMINA**

<table>
<thead>
<tr>
<th>Properties of Dried Bars</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (gm/cc)</td>
<td>2.7</td>
<td>2.7</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>% Theoretical Density</td>
<td>68</td>
<td>68</td>
<td>66</td>
<td>66</td>
</tr>
<tr>
<td>% Linear Shrinkage</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Modulus of Rupture (psi)</td>
<td>230</td>
<td>220</td>
<td>190</td>
<td>230</td>
</tr>
</tbody>
</table>

### TABLE XIII

**CHARACTERISTICS OF WATER MILL ED ALUMINA**

<table>
<thead>
<tr>
<th>Slip Properties</th>
<th>Slip No. 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.2</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.18</td>
</tr>
<tr>
<td>pH-Aged 2 days</td>
<td>Slip would not flow</td>
</tr>
<tr>
<td>Casting Properties</td>
<td></td>
</tr>
<tr>
<td>Casting Time (Min.)</td>
<td>30</td>
</tr>
<tr>
<td>Nature of Freshly Cast Bars</td>
<td>Sl. Thixotropic</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Properties of Dried Bars</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (gm/cc)</td>
<td>2.4</td>
</tr>
<tr>
<td>% Theoretical Density</td>
<td>61</td>
</tr>
<tr>
<td>% Linear Shrinkage</td>
<td>3</td>
</tr>
<tr>
<td>Modulus of Rupture (psi)</td>
<td>70</td>
</tr>
</tbody>
</table>
Figure 33. Particle Size Distributions of Alumina Slips.
The most satisfactory slips developed were those obtained through acid milling. These slips gave cast bars with very good dried strength, deteriorated little on ageing, and gave excellent surface finishes. The slips prepared from the dry milled alumina and the water milled slip deteriorated too rapidly to be of practical value. In addition, the water milled slip required such a large volume of water to yield a suitable milling slurry that the resulting slip had a very low solid concentration.
All slips, except the one prepared with 0.9 N hydrochloric acid, increased in pH upon being aged for two days at room temperature. This increase would be expected to result from the reactions between hydrochloric acid and the amphoteric aluminum compounds.

The thixotropic behavior of the bars cast from slips having pH values below 4.0 was associated with the tendency of these slips to remain flocculated. Casting from such a flocculated slip should be expected to lead to a cellular structure subject to collapse on mechanical disturbance, hence thixotropy. In the same way, the cellular collapse during drying should lead to higher drying shrinkage. This correlation of thixotropy and drying shrinkage was observed in the study.

The modulus of rupture of dried bars cast from the slips compared most favorably with that of dried bars cast from silica (180 psi). The lower dried strength of the bars cast from the water ground slip was to be expected from the low densities of these bars.

An extensive study of the fired slip cast alumina has not yet been made. A few 0.375-inch diameter bars were fired at about 3100°F for one hour in an oxy-acetylene PCE furnace. These bars showed fired densities in excess of 85 per cent of theoretical and moduli of rupture in excess of 20,000 psi.
C. THERMET FUELS

Investigations were begun to explore the formation of refractory fuels by exothermic reactions. These investigations will be reported in a separate classified report in view of the Category III classification applied to this phase of the contract.
IV. DISCUSSION

As in the previous work, the strength-temperature curves obtained from firing studies of the silica correspond closely in appearance to ordinary precipitation strengthening processes. Attempts to concretely correlate the silica bonding mechanism with second-phase precipitation processes have not yet met with success. The indications of preferred orientation of cristobalite during devitrification do, however, support the proposed picture of particle bonding by cristobalite growth. If devitrifying silica forms an oriented crystalline phase on the surface of each particle, an increase in the tendency of cross-particle cristobalite growth would be expected in view of the lattice harmony in the two contacting surfaces. Attempts are planned to confirm this by electron diffraction from fractured particle faces.

The statistical study of the fabrication variables associated with the slip casting of silica proved useful in predicting the results which other agencies working with silica might expect. The strong dependence of the reproducibility of strengths obtained with the silica on the nature of the slip and the firing conditions was naturally anticipated. This dependence would be implied by a recognition that a difference in the particle size distribution of the slip would be reflected in a different degree of particle surface contact in the casting, hence a different bonding tendency and a different degree of reproducibility. In the same manner, the extent of bonding would depend on the time allowed for atom movement at temperature since the bonding, whether by sintering, cross-particle cristobalite growth, or any other mechanism, is obviously a kinetic process. The importance of the study, however, is in the implication that the reproducibility of results is relatively insensitive to differences in the technique of the operator. This would indicate that any worker who is familiar with the usual techniques
of slip casting should be capable of achieving results similar to those in this report with little difficulty.

The tendency of the slip cast fused silica to increase in strength with temperature was again noted in the current work. The most obvious possibility for explaining this observation would be that of onset of plastic deformation of the silica at elevated temperatures. Such an occurrence would be expected to decrease the problems of warping and alignment of the silica and to allow a more full realization of its true strength. This possibility could be further examined by the performance of creep tests on the silica. Such tests are planned for the future.

The tracer gas permeation system continued to meet expectations for successful use. Mathematical confirmation of its validity permits the method to be placed in the category of general research methods since the equations developed allow prediction of behavior with any material.

The discovery of the contamination resulting from the firing of silica in contact with Keltex has provoked a review of the study of the devitrification of silica. The possibility of acceleration of devitrification by the surface contaminants could explain the differences in the current rate studies and those of Verduch (1). In future rate determinations, x-ray fluorescence will be carried out on all samples to insure that the surface calcium content is no higher than that of the unfired slip. This precaution, along with elimination of platinum deposition on the sample, should improve reproducibility of the high temperature x-ray runs.

V. PERSONNEL

The work discussed in this report was conducted in the Ceramics Branch, Mr. J. D. Walton, Head. The project was directed by Dr. J. D. Fleming with Mr. J. W. Johnson acting as Assistant Project Director. Major contributing personnel were:

- Dr. R. F. Hochman, Research Associate
- Mr. J. N. Harris, Assistant Research Engineer
- Mr. S. H. Bomar, Group Leader
- Mr. A. R. Colcord, Group Leader
- Mr. R. C. Farmer, Graduate Research Assistant
- Mr. Jude Koenig, Research Assistant
- Mr. R. H. Bentley, Technician
- Mr. C. E. Burnett, Technician
- Mr. R. K. Butz, Technician
- Mr. J. L. Carroll, Technician
- Mr. P. A. Darius, Technician
- Mr. W. B. Moore, Technician
- Mr. D. H. Slayton, Technician
- Mr. F. D. Thackston, Technician

Submitted

J. D. Fleming
Senior Investigator

J. W. Johnson
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Frederick Bellinger, Chief
Material Sciences Division

J. D. Walton, Head
Ceramics Branch

Approved:
UNCLASSIFIED

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

PROGRESS REPORT NO. 2
Part 2. (Declassified)
Project No. B-153

MATERIALS FOR
HIGH TEMPERATURE NUCLEAR ENGINEERING APPLICATIONS

By
J. D. FLEMING and J. W. JOHNSON

CONTRACT NO. AT-(40-1)-2483
U. S. ATOMIC ENERGY COMMISSION

15 AUGUST 1959 to 15 AUGUST 1960

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

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of the Georgia Institute of Technology
Atlanta, Georgia

PROGRESS REPORT NO. 2
Part 2. (Declassified)
Project No. B-153

MATERIALS FOR
HIGH TEMPERATURE NUCLEAR ENGINEERING APPLICATIONS

By
J. D. FLEMING and J. W. JOHNSON

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CONTRACT NO. AT-(40-1)-2483
U. S. ATOMIC ENERGY COMMISSION
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15 AUGUST 1959 to 15 AUGUST 1960

UNCLASSIFIED
The investigation reported herein was performed by the Engineering Experiment Station of the Georgia Institute of Technology under U. S. Atomic Energy Commission Contract No. AT-(40-1)-2483. This work was sponsored by the Division of Reactor Development, Fuels and Materials Development Branch, Mr. Julius M. Simmons, Chief. The contract was administered by the Oak Ridge Operations Office, Reactor Division, Dr. David F. Cope, Director.

This report covers the progress made under Phase IV of the contract during the period from 15 August 1959 to 15 August 1960. The material contained in this report has been reviewed and declassified by the Division of Classification.
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I. INTRODUCTION

With the growing interest in nuclear propulsion, desired operating temperatures for reactors are steadily increasing. As the operating temperature increases, much higher fabrication temperatures become necessary and forming costs and technical difficulties increase out of proportion. One method of avoiding the necessity of material fabrication at ultrahigh temperatures would be using internally generated heat to sinter the desired refractory products of exothermic reactions. Phase IV of Contract No. AT-(40-1)-2483 is intended to explore the application of such an approach to the generation of practical fuel materials.
II. SUMMARY

Exploratory investigations were begun to examine the possibilities of forming refractory fuel mixtures, called thermets for convenience, through exothermic reactions.

Systems were designed and constructed to permit differential thermal analysis and thermogravimetric analysis of the thermets in inert or oxidizing atmospheres.

Simple thermet reductions of uranium dioxide by aluminum or beryllium were given preliminary study. Although indications of reactions below 2000°F were obtained, the mechanism of the reactions was not established.
III. EXPERIMENTAL WORK

1. Differential Thermal Analysis System

An inert atmosphere differential thermal analysis system was constructed to supplement existing equipment. The heating rate control is furnished by a Minneapolis Honeywell cam control with variable cam speed, giving heating rates from 2.5 to 120°F per minute. The cam control furnishes the input to a Minneapolis Honeywell magnetic amplifier which controls a General Electric saturable core reactor rated at 3 kva. The temperature of the standard pellet and the temperature differential are recorded by a Moseley X-Y recorder.

The control panel is furnished with quick connect fittings so that any number of furnaces may be used interchangeably. This eliminates the delay involved in cooling the furnace between runs. The furnaces are heated by Kanthal resistance coils held in slip cast fused silica cores. The heating chambers are insulated by fused silica foam with a thermal conductivity of approximately 0.1 BTU/hr. ft. °F. Inconel clad, magnesia insulated platinum-platinum 13 per cent rhodium Minneapolis Honeywell or Thermo Electric thermocouples are used. The standard, unknown, and control thermocouples are arranged on a circle for the most representative temperature control.

A block diagram of the DTA system is shown in Figure 1. A schematic of the electrical system and measuring circuit is shown in Figure 2. The furnace is shown in Figure 3. Figure 4 shows a photograph of the control panel and furnace.

2. Thermogravimetric Analysis System

An electronic balance, produced by the Minneapolis Instrument Company, was purchased for use in a recording thermogravimetric system. Provisions are made for the balance and balance furnace to be connected to the control
Figure 1. Block Diagram of DTA System.
Figure 2. Schematic Diagram of DTA Electrical and Measuring Circuits.
Figure 3. Diagram of DTA Furnace.
Figure 4. DTA Control Panel and Furnace.
console of the differential thermal analysis system. This permits the system to be used not only to determine constant temperature weight changes, such as oxidation rates, but also for thermogravimetric analysis. The furnace used for TGA runs is of the same design as the DTA furnace shown in Figure 3. The same control thermocouple is used, as with DTA and either an Inconel, alumina, or silica cup is suspended in the furnace to hold the TGA specimen.

3. Thermet Reactions

Several simple reactions were chosen for initial study. These reactions and the accompanying standard free energy changes (1) were:

1. \( \frac{1}{2} \text{UO}_2 + \text{Be} \rightarrow \frac{1}{2} \text{U} + \text{BeO} \)
   \[ \Delta F_{298} = -12,800 \text{ cal} \]

2. \( \frac{3}{4} \text{UO}_2 + \text{Al} \rightarrow \frac{3}{4} \text{U} + \frac{1}{2} \text{Al}_2\text{O}_3 \)
   \[ \Delta F_{298} = -3,700 \text{ cal} \]

3. \( \frac{1}{2} \text{U}_3\text{O}_8 + \text{Be} \rightarrow \frac{3}{2} \text{UO}_2 + \text{BeO} \)
   \[ \Delta F_{298} = -104,000 \text{ cal} \]

4. \( \frac{3}{4} \text{U}_3\text{O}_8 + \text{Al} \rightarrow \frac{9}{4} \text{UO}_2 + \frac{1}{2} \text{Al}_2\text{O}_3 \)
   \[ \Delta F_{298} = -140,500 \text{ cal} \]

The variation with temperature of heats and free energies of reaction for these reactions is shown in Figure 5 through 8.

A safety evaluation was made of thermets in the above systems by pressing stoichiometric pellets and heating them in a muffle furnace to determine the rough ignition temperature. \text{UO}_2-\text{Be} mixtures were observed, through a sight hole in the furnace, to ignite at about 1700°F and rapidly approach a brilliant
Figure 5. Heat and Free Energy of Reaction, \( \frac{1}{2} \text{UO}_2 + \text{Be} = \frac{1}{2} \text{U} + \text{BeO} \).
Figure 6. Heat and Free Energy of Reaction, \( \frac{3}{4} \text{UO}_2 + \text{Al} = \frac{3}{4} \text{U} + \frac{1}{2} \text{Al}_2\text{O}_3 \).
Figure 7. Heat and Free Energy of Reaction, $\frac{1}{2} \text{U}_3\text{O}_8 + \text{Be} = \frac{3}{2} \text{UO}_2 + \text{BeO}$. 
Figure 8. Heat and Free Energy of Reaction, $\frac{3}{4} \text{U}_3\text{O}_8 + \text{Al} = \frac{9}{4} \text{UO}_2 + \frac{1}{2} \text{Al}_2\text{O}_3$. 
white heat. During the firing in air, the pellets began oxidizing and crumbled following the reaction. The pellets showed no apparent tendency to undergo catastrophic oxidation prior to or during the reaction. This was taken to indicate that metallic uranium was formed through exothermic reduction of the oxide and then re-oxidized, leading to decomposition of the pellet.

Table I shows semi-quantitative spectrographic analyses of the powders used in the thermet studies. In all of the initial test runs, Davison ceramic uranium dioxide was used.

**TABLE I**

<table>
<thead>
<tr>
<th></th>
<th>Davison Ceramic UO₂</th>
<th>Spencer Fused UO₂</th>
<th>Brush BeO Grade I</th>
<th>Brush Be</th>
<th>Alcoa #140 Al</th>
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<tbody>
<tr>
<td>Aluminum</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.007</td>
<td>0.007</td>
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</tr>
<tr>
<td>Barium</td>
<td>0.003</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boron</td>
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<td>0.00003</td>
<td>0.00003</td>
<td></td>
<td>0.003</td>
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<tr>
<td>Cadmium</td>
<td>0.00006</td>
<td>0.00008</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Calcium</td>
<td></td>
<td></td>
<td>0.006</td>
<td>0.0007</td>
<td>0.003</td>
</tr>
<tr>
<td>Chromium</td>
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<td>0.0008</td>
<td></td>
<td></td>
<td>0.0007</td>
</tr>
<tr>
<td>Copper</td>
<td>0.005</td>
<td>0.00003</td>
<td>0.003</td>
<td>0.003</td>
<td>0.08</td>
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<tr>
<td>Iron</td>
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<td>0.008</td>
<td>0.007</td>
<td>0.003</td>
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<td>Lithium</td>
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<td>0.0003</td>
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<tr>
<td>Magnesium</td>
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<tr>
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<tr>
<td>Molybdenum</td>
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<td>0.003</td>
<td>0.0003</td>
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(Continued)
Particle size distributions, obtained from a Coulter Counter, are shown in Figures 9 through 11 for the beryllium, aluminum, and ceramic uranium dioxide powders used in the thermet work.

Surface areas were determined by nitrogen adsorption for the thermet powders. These values are given in Table II.

### TABLE II

**SURFACE AREAS OF THERMET POWDERS**

<table>
<thead>
<tr>
<th>Powder</th>
<th>Surface Area (m²/gm)</th>
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<tr>
<td>Brush Beryllium</td>
<td>0.39</td>
</tr>
<tr>
<td>Alcoa No. 140 Aluminum</td>
<td>1.10</td>
</tr>
<tr>
<td>Davison Ceramic Uranium Dioxide</td>
<td>1.80</td>
</tr>
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</table>
Figure 9. Particle Size Distribution of Alcoa No. 140 Aluminum.
Figure 10. Particle Size Distribution of Brush Beryllium.
Figure 11. Particle Size Distribution of Davison Ceramic Grade Uranium Dioxide.
Progress Report No. 2, Project No. B-153

Electron micrographs of the beryllium and ceramic uranium dioxide are shown in Figure 12.

Optical micrographs of the thermet powders are shown in Figure 13.

Pellets of the UO$_2$-Be mixture were fired and cooled in a tube furnace in argon. The pellets remained intact and appeared to have fired. Several were sectioned with a diamond saw and mounted for microscopic examination. Figure 14 shows cross sections of these pellets. The structure appeared quite dense and free of blow holes. The pellets were quite easy to saw and did not splinter or fragment nor did they undergo obvious warping during firing.

Following completion of the new DTA system, initial analyses were made of pellets pressed from the stoichiometric UO$_2$-Be mixture at a heating rate of 20°F per minute. Ignition occurred in all cases at about 425°F in contrast to the previous firing at 1700°F. In addition, only a small exothermic peak was observed as opposed to the apparently high energy evolution observed with the furnace firing. No explanation for this anomalous behavior was found. The only suggestion with apparent validity would be the existence of a temperature dependent induction period for the reaction. If this were the case, the more rapid heating resulting from firing in a muffle furnace at temperature might be expected to increase the pellet temperature to a high level before the induction period could be passed. The slower heating rate in the DTA test would be likely to result in lower temperature firing. Firing at a higher temperature would result in a faster reaction rate and a more nearly instantaneous release of the energy of the reaction. The reaction would thus appear to the observer to be more highly exothermic although the heat of reaction changes little with temperature. DTA runs at higher heating rates were begun to further explore this possibility.

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Figure 12. Electron Micrographs of Thermet Powders.
Figure 13. Optical Micrographs of Thermet Powders. (550X)
Figure 14. Cross Sections of Uranium Dioxide - Beryllium Thermets. (7-1/2X)
X-ray diffraction was unable to identify the phases in the thermets because of uranium heavy atom interference. Polyvinyl alcohol films were formed on surfaces of the fired thermets and stripped off. Selected area electron diffraction patterns were taken on particles torn from the thermet with the films. Patterns were also made on all the powders used in the study as well as the oxidized forms of the powders. The patterns from the thermets did not correspond to any of the known patterns. Efforts to identify the thermet patterns have not yet been successful.

Unfired pellets and pellets fired in argon and air were sectioned and subjected to microscopic examination. Representative samples are shown in Figure 15.

Initial TGA check runs were made using beryllium-uranium dioxide thermet pellets which had a firing point of approximately 450°F in air as determined by DTA. The pellets were subjected to TGA firing in air. The sensitivity of the balance was such that an oxidation of approximately 0.9 per cent of the beryllium or a conversion of the urania, initially UO$_2$.04, to UO$_2$.06 could be detected. No weight change could be detected during firing of the pellets, at a 20°F per minute rate of rise, or prior to a post-firing temperature of approximately 600°F. At 600°F a weight gain of 3.4 per cent was detected following which the pellet crumbled and was partially lost from the weighing capsule. Though not conclusive, these observations would seem to indicate that a reduction caused the DTA peak since no weight change, indicative of simple air oxidation, was noted during firing.
Figure 15. Micrographs of Uranium Dioxide - Beryllium Thermets. (267X)
IV. DISCUSSION

The initial investigations of the thermitic reduction of uranium dioxide by beryllium and aluminum indicated that reactions do occur at temperatures below 2000°F. The exact nature and mechanism of the reactions was obscured by the presence of excessive amounts of oxygen, even in the inert gas runs, because of defective furnace design.

Some indications were obtained that the reduction of uranium dioxide by beryllium would occur only if preceded by partial oxidation of the uranium dioxide. The reduction of the oxidized uranium dioxide, in a more thermodynamically favorable reaction, could serve as an exothermic "trigger" reaction for the reduction of the unoxidized dioxide. DTA runs in a vacuum system, now under construction, should serve to clarify this point.
V. PERSONNEL

The work discussed in this report was conducted in the Ceramics Branch, Mr. J. D. Walton, Head. The project was directed by Dr. J. D. Fleming with Mr. J. W. Johnson acting as Assistant Project Director. Major contributing personnel in Phase IV were:

- Mr. S. H. Bomar, Group Leader
- Mr. C. E. Burnett, Technician
- Mr. R. K. Butz, Technician
- Mr. F. D. Thackston, Technician

Submitted by:

J. D. Fleming
Senior Investigator

J. W. Johnson
Assistant Project Director

Approved:

J. D. Walton, Head
Ceramics Branch

Frederick Bellinger, Chief
Material Sciences Division
SUMMARY REPORT NO. 1
Project No. B-153

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U. S. ATOMIC ENERGY COMMISSION

1 JUNE 1961 to 1 JUNE 1962

Engineering Experiment Station
Georgia Institute of Technology
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1 JUNE 1961 to 1 JUNE 1962
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FOREWORD

The investigation reported in this document was performed by the Engineering Experiment Station of the Georgia Institute of Technology under U. S. Atomic Energy Commission Contract No. AT-(40-1)-2483. The work was sponsored by the Division of Reactor Development, Fuels and Materials Development Branch, Mr. J. M. Simmons, Chief. The contract was administered by the Oak Ridge Operations Office, Reactor Division, Dr. David F. Cope, Director.

Prior to the current contract year, Summary Reports were not submitted. Consequently, although this report is entitled Summary Report No. 1, several prior reports have been distributed. For a listing, see Section VII.

This report covers the period from 1 June 1961 to 1 June 1962.
I. INTRODUCTION

The excellent thermal shock resistance and indications of good radiation resistance of fused silica have recommended it for consideration for use in high temperature radiation fields. With the development at Georgia Tech of techniques for economical fabrication of large and complex silica shapes by slip casting, major objections to this material, on the basic of cost and fabrication difficulty, have been overcome.

Although the art of fused silica is well developed, many gaps are still existent in its science. Insufficient data are available for the intelligent evaluation of fused silica as a reactor material. One object of Project B-153 is the development of sufficiently reliable data for, and basic understanding of, fused silica to permit this evaluation.

Fused silica is unique among slip casting materials in the small amount of drying and firing shrinkage associated with its fabrication. If other materials could be caused to display a similarly low shrinkage, much better advantage could be taken of slip casting as a fabrication technique. A second object of Project B-153 is the optimization of slip casting ceramics, through a comparison of silica with different materials and a basic study of the mechanism of slip casting. Slip cast alumina is being investigated at present.

The competitiveness of nuclear power systems depends strongly on the extent to which use can be made of potentially high operating temperatures. The fuels required to operate stably at these high temperatures must be fabricated at equally high temperatures if conventional fabrication techniques are used. The fabrication problems and expense increase with fabrication temperature in more than linear proportion, adversely affecting the economics of the system.
Project B-153 also is concerned with an investigation of a novel fabrication process in which the material being fabricated furnishes the high fabrication temperatures required. This process consists of selecting materials which will undergo highly exothermic chemical reactions, producing both high temperatures and desirable reaction products. To date, aluminum and beryllium reduction of oxides of uranium have been studied, with the major emphasis being placed on aluminum reduction of $\text{U}_3\text{O}_8$. Since Al-$\text{U}_3\text{O}_8$ dispersions are in common use as reactor fuels, the results of this study are obviously of interest in hazards evaluation. The program is planned so as to yield information in a form suitable for this evaluation.
II. SUMMARY

Devitrification rates were determined in a high temperature x-ray diffraction unit using samples cast in three types of plaster with two types of mold release. For routine work, the plaster and mold release influences were small enough to be ignored. For highly critical work, U. S. Gypsum Puritan plaster and a graphite mold release should be used in view of a slightly lower devitrification rate. Keltex mold release proved preferable in routine work with molds not having close draws since the Keltex film added some strength to the green casting.

A system was designed to measure the porosity, bulk density, and theoretical density of porous specimens by air displacement. The system does not require immersion of the sample in a liquid in any step. Comparisons were made of the air displacement test with a water displacement test performed according to ASTM C-20-46. The air displacement method proved faster, more sensitive, more accurate, and less subject to operator differences than the water displacement method. The water test was capable of showing representative qualitative changes in the silica upon firing provided great care was exercised. The water test was quantitatively inaccurate even under optimum conditions.

Estimation of a firing correction time for the silica proved possible using the porosity data. This correction time accommodated the changes in the silica occurring during heating to the soaking temperature. The actual heat-up time was found to be suitable for use as the correction time in the temperature range studied. The use of this correction time permitted the properties of the dried cast silica to be correlated with the fired properties.
The porosity of slip cast fused silica was measured by air displacement as a function of firing conditions. The minimum porosity reached ranged from 13.93 to 14.37 per cent. The firing time for minimum porosity ranged from two hours at 2300°F to 46.3 hours at 2100°F. Use of the time for minimum porosity as a normalizing factor permitted good correlation of all the porosity data.

The modulus of rupture of slip cast fused silica was measured as a function of firing conditions. The maximum strength was in the range 4500 - 4700 psi for all firing temperatures from 2100 to 2300°F. The firing time for maximum strength was about the same as the time for minimum porosity at 2100°F but was slightly shorter at higher firing temperatures. This indicates a greater dependence of strength on cristobalite fracture during post-firing cooling than that shown by porosity.

A study was made of the compressive strength of slip cast fused silica. The crushing strength showed less dependence on internal flaws than did the modulus of rupture. As a result, the firing times for maximum crushing strength were somewhat longer than for maximum modulus of rupture. The maximum crushing strength was approximately 26,000 psi.

Further statistical analyses of the firing procedure for silica tensile test rings showed that the data scatter was principally due to vertical temperature gradients in the furnace. Since funds were not available for reconstruction of the furnace, the sample size was increased and the number of conditions to be studied was decreased. Initial results from the elevated temperature tensile tests showed that the tensile strength of slip cast fused silica fired at 2100°F for 16.3 hours increased from 3800 psi at room temperature to 6400 psi at 2000°F.
Investigations were made of the influence of firing atmosphere on the properties of slip cast fused silica. The initial studies showed that steam had a striking effect on the fired strength and porosity as well as the expected effect on devitrification rate. The modulus of rupture reached in steam firing was greater than 5400 psi at 2200°F compared with 4200 psi for air firing. The maximum strength in steam firing was developed in less than half the time required in air firing. The minimum porosity reached in steam firing was 10.14 per cent compared with 14.63 in air firing. Devitrification in steam firing was five to ten times as rapid as in air firing. Firing in argon markedly decreased the rates of strengthening, porosity decrease, and devitrification. The modulus of rupture was only 1420 psi after 16 hours at 2200°F.

The Kr-85 permeation system was completed and check runs were begun. Three replicate runs on a single sample indicated effective diffusivities with a maximum deviation of 3.5 per cent from the average.

Alumina casting slips were developed by wet and dry milling of Norton Type 38 Alundum. These slips had solids contents of 82.1 w/o at an apparent viscosity of 2500 - 2700 cp. Studies were made of the influence of mold vibration and pressure application on the casting rate of the alumina slips. An axial 60 cps vibration with an amplitude of 0.015-in. increased the casting time but improved the cast density and strength. Pressure application of 60 psig decreased the casting time by a factor of four with an improvement in the soundness of the casting and only a moderate decrease in the case density. Alumina bars cast with vibration and pressure were fired at temperatures of 2030 to 2250°F for 8 hours. The bars fired at 2250°F showed an air displacement porosity of 28.1 per cent, a firing shrinkage of 1.97 per cent, and a
modulus of rupture of 17,000 psi. Bars fired for 2 hours at 3100° F showed an air displacement porosity of approximately 1 per cent and a modulus of rupture of approximately 30,000 psi.

The apparent theoretical density of the U₃O₈ used in the studies of Al-U₃O₈ interactions was measured by air displacement and in a Beckman air pycnometer. The air displacement value was 8.11 ± 0.03 gm/cc and the air pycnometer value was 8.16 ± 0.01 gm/cc.

The particle size of the U₃O₈ used in the pellets markedly influenced the thermet ignition characteristics. Ignition temperatures decreased from 1920° F with +140 mesh U₃O₈ to 1790° F with -325 mesh U₃O₈. The DTA peak height and peak area increased with decreasing particle size to 270 mesh and then decreased upon a further particle size decrease.

Studies were begun to elucidate the influence of aluminum content on the Al-U₃O₈ interactions. X-ray analyses indicated definite reactions in pellets containing 31.5 w/o aluminum or more by 1200° F and in pellets with 26.6 w/o aluminum or more by 1400° F. In most cases, these lower temperature reactions were incomplete, yielding some UO₂ but no aluminum-uranium intermetallic compounds. In one pellet containing 60 w/o aluminum, however, a complete reaction was detected at 1200° F with the formation of UA₁₄.

Electron beam microprobe analyses were made of fired composites containing 14.6 w/o aluminum. Constituents detected were a-Al₂O₃, UO₂, and UA₁₂.

Several thermochemical calculations were made to indicate the maximum energy release which might be expected from reacting Al-U₃O₈ composites. These calculations predicted a maximum specific release of approximately 1.2 Mw·sec per kg of fuel at a fuel composition of 25-35 w/o aluminum.
Several motion pictures and still photographs were made of igniting 14.6 w/o aluminum composites. These pictures showed the ignition to be completed in approximately 0.1 sec. in a 3/8-in. diameter pellet 1/2-in. long.

Be-U₃O₈ compacts containing 7.9 w/o of -325 mesh beryllium were subjected to differential thermal analysis. The samples ignited sharply at 1820° F. The reaction appeared more vigorous than the corresponding Al-U₃O₈ reactions. No evidence was found of a low temperature reaction similar to that in the Al-U₃O₈ composites.
III. EXPERIMENTAL WORK

A. Slip Cast Fused Silica

1. Slip Characteristics

The fused silica slip used in this investigation was produced by Glasrock Products\textsuperscript{1}. The properties of the slip are summarized in Table I and Figure 1.

<table>
<thead>
<tr>
<th>TABLE I</th>
</tr>
</thead>
<tbody>
<tr>
<td>PROPERTIES OF FUSED SILICA SLIP</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Weight Per Cent Solids</th>
<th>82.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent Viscosity</td>
<td>131  cp.</td>
</tr>
<tr>
<td>pH</td>
<td>5.2</td>
</tr>
</tbody>
</table>

2. Devitrification Studies

A Kanthal wound furnace (P3)\textsuperscript{2} was used in a high temperature x-ray diffraction unit (P1) to investigate the influence of the casting plaster and mold release on the devitrification of slip cast fused silica. Samples, 1 x 2 x 0.2-cm, were cast from the slip using three types of plaster and two types of mold release. The plasters were U. S. Gypsum No. 1 and Puritan and Bestwall K-59. The mold releases were Keltex, manufactured by the Kolco Company, and

\textsuperscript{1}Glasrock Products, Inc., 1101 Glidden Street, Atlanta 18, Georgia

\textsuperscript{2}Numbers in parentheses refer to prior reports in which more detailed information will be found. P1, P2, and P3 represent Progress Report No. 1 (1959), No. 2 (1960), and No. 3 (1961). Q1 represents Quarterly Report No. 1 (April 1962).
Figure 1. Particle Size Distribution of Fused Silica Slip.
a graphite suspension developed under this contract (P2). These samples were heated to 2200° F in the diffraction furnace and the devitrification rates were determined by making repeated scans of the cristobalite (101) plane. The results of these tests are shown in Figure 2. Unless noted, the samples cast with Keltex were stripped of the Keltex film before being fired.

In studies of the influence of the type of plaster and mold release on the strength of slip cast fused silica, no statistically significant effect was noted. The obvious conclusion is that, for most work, any of the three plasters will be suitable and either Keltex or graphite may be used as long as the Keltex is removed before firing. This precaution is unnecessary with graphite. Other observations of importance are that the Keltex film lends some strength to the green casting but may tend to roll and prevent release in close mold draws and that the graphite gives unexcelled release properties but adds no strength to the green casting. Keltex is recommended for casting in relatively open molds which may be separated for removal of the casting while graphite is recommended for molds which cannot be separated or which have close draws.

While all three plasters are suitable for routine work, the lower devitrification rate obtained from Gypsum Puritan may recommend it for use in casting parts for service in critical areas.

Attention is directed to the fact that the devitrification curves in Figure 2 are for the surface of the casting only. Since the finer particles are drawn to the surface during casting and since devitrification rate is qualitatively proportional to the specific particle surface area, the surface rate of devitrification will be much higher than that of the bulk of the sample. The bulk devitrification rate at 2200° F (P1) is approximately seven times slower than the surface rate.
Figure 2. Extent of Surface Devitrification at 2200°F as a Function of Casting Conditions.
3. Air Displacement Porosimeter

Development of an air displacement porosimeter has been of incalculable value in several phases of this program. Rapid, reproducible, and accurate determinations of porosity, bulk density, and theoretical density have been made possible even with unfired samples.

The porosimeter (P3) is shown in Figures 3 and 4. The system operates by displacement of known volumes of air into the voids of the sample and into the space in a chamber, of known volume, remaining after insertion of the sample whose surface is sealed by a vinyl film. The sample void and bulk volumes read directly from the scales of the porosimeter are used with the sample weight to calculate the packing properties. Since the sample is never immersed in a liquid, it remains uncontaminated and green samples which would normally be destroyed by liquid immersion may be tested as easily as fired samples.

Results from the air displacement system were compared with those from water displacement tests per ASTM C-20-46. Twenty standard 3/4-inch diameter silica bars, 5-1/2 inches long, were cast and fired at 1500 °F for two hours. This low firing condition was used in order to provide sufficient strength for handling but to minimize sample to sample variations. Each bar was run three times using both test methods. Two runs were made by one investigator and one by a second investigator. The averaged results are shown in Table II.

The data shown in Table II indicate that the air displacement method and water displacement method lead to essentially the same bulk volume values. The ability of air to penetrate small pores in the sample which would appear opaque to water leads to higher porosity and theoretical density values. The time required per sample was much less for the air displacement method.
Figure 3. Air Displacement Porosimeter.
Figure 4. Sample Platform for Air Displacement Porosimeter.
### TABLE II

**COMPARISON OF AIR AND WATER DISPLACEMENT POROSITY TESTS**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Technician A</th>
<th>Technician B</th>
<th>Overall Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Run 1</td>
<td>Run 2</td>
<td></td>
</tr>
<tr>
<td>porosity (AD)*</td>
<td>16.36%</td>
<td>16.33%</td>
<td>16.34%</td>
</tr>
<tr>
<td>porosity (WD)</td>
<td>14.09%</td>
<td>14.01%</td>
<td>13.90%</td>
</tr>
<tr>
<td>bulk Volume (AD)</td>
<td>43.34 cc</td>
<td>43.34 cc</td>
<td>43.33 cc</td>
</tr>
<tr>
<td>bulk Volume (WD)</td>
<td>43.36 cc</td>
<td>43.36 cc</td>
<td>43.33 cc</td>
</tr>
<tr>
<td>Apparent Theoretical Density (AD)</td>
<td>2.237 gm/cc</td>
<td>2.234 gm/cc</td>
<td>2.235 gm/cc</td>
</tr>
<tr>
<td>Apparent Theoretical Density (WD)</td>
<td>2.177 gm/cc</td>
<td>2.173 gm/cc</td>
<td>2.172 gm/cc</td>
</tr>
<tr>
<td>Total Time Per Bar (AD)</td>
<td>-</td>
<td>5.3 min.</td>
<td>-</td>
</tr>
<tr>
<td>Total Time Per Bar (WD)</td>
<td>-</td>
<td>12.0 min.</td>
<td>-</td>
</tr>
</tbody>
</table>

*AD = air displacement

*WD = water displacement

All values are averages for 20 specimens.

A statistical analysis of the data was made (P3). This analysis indicated:

1. The air displacement system is capable of showing much smaller sample differences than the ASTM C-20-46 test.

2. The air displacement system is far less sensitive to operator differences than ASTM C-20-46.
3. Systematic differences occur in porosity and bulk volume measurements made by different operators using ASTM C-20-46. This does not occur with the air displacement tests.

4. ASTM C-20-46 leads to systematically lower porosities and theoretical densities than the air displacement test.

Determinations made in the past by water displacement and by air displacement showed both qualitative and quantitative differences in the profiles of the porosity of slip cast fused silica as a function of firing conditions. The statistical study (P3) indicated that the qualitative differences resulted from the significant operator dependence of the water test. In order to verify this implication, before relying too heavily on the air displacement test, one further study was made.

Sets of ten slip cast silica bars, 3/4-inch in diameter by 5-5/8-inch long, were fired at 2200°F for 2, 4, 6, and 16 hours. The fired samples were dried for 16 hours at 230°F and cooled in a desiccator to room temperature before being tested. The porosities of the bars were then measured, first using air displacement and then by water displacement. All water displacement tests were made on the same day and by the same technician in order to eliminate the operator effects insofar as possible. This precaution and that of drying the bars before testing were not taken in the previous porosity profile determinations by water displacement.

The results of the air and water determinations are shown in Figure 5.1 These results indicate that the two tests are capable of showing qualitative porosity changes equally as well provided more than the usual care is taken

1The porosity of the unfired bars could not be determined by water displacement since the green structure could not withstand boiling.
Figure 5. Porosity Profiles at 2200°F from Water Displacement and Air Displacement.
in applying the water method. Even under these circumstances, however, the water displacement test may introduce a qualitative error if a small surface pore size exists in the sample under some firing conditions and not under others. In any case, the water absorbed into the sample will be unable to penetrate all the pores, resulting in a lower porosity value than is obtained by air displacement. A quantitative error in the water absorption method appears unavoidable.

4. Porosity and Density

a. Correction of Firing Time

Prior to development of the air displacement porosimeter, all firing tests using slip cast fused silica were correlated using the time measured from the time at which the preheated furnace returned to temperature following insertion of the samples. Since the samples would obviously undergo changes during the reheat time, this time base line provided poor correlation particularly with reference to the unfired properties. No attempt was made in the past to correct the firing time since the strengths showed too much scatter to provide a statistically reliable correction factor. The air displacement porosimeter, however, provided a suitable estimate of the correction time \( Q_1 \). This correction time proved to be satisfactorily given by the actual reheat time. All corrected time correlations given for the fired properties of the slip cast fused silica are thus given by the time following insertion of the samples into the furnace.

b. Bulk Properties

Sets of 20 3/4-in. diameter by 5-5/8-in. long bars were cast from fused silica and fired at 2000, 2100, 2133, 2166, 2200, and 2300° F for various times.
The bulk density, porosity, and theoretical density values were determined by air displacement. The bulk density and porosity are shown as a function of corrected firing time in Figures 6 and 7.

The minimum porosity values in Figure 7 were obtained using four point Lagrangian interpolation. The time at which the minimum porosity is reached can be corrected by the equation

$$\log \theta_m = 15.265 - 6.539 \times 10^{-3} T$$

where

$$\theta_m = \text{corrected firing time to reach minimum porosity, hr.}$$

$$T = \text{firing temperature, °F.}$$

This equation, obtained by applying least squares to the interpolated data, is shown in Figure 8.

It is interesting to note that the corrected firing time for minimum porosity may be used as a correlating factor by means of a reduced firing time, $\theta_r$, defined by

$$\theta_r = \frac{\theta}{\theta_m}$$

The porosity is shown as a function of reduced firing time in Figure 9.

5. Modulus of Rupture

The firing behavior of slip cast fused silica was further clarified by extending the lower temperature firings to longer times and by firing at closer temperature intervals. Three-quarter-in. diameter by 5-5/8-in. long bars were slip cast in one piece molds using the graphite mold release.
NOTE: The shaded area associated with a given point represents the region which is expected to contain that point with 95 per cent confidence.

Figure 6. Bulk Density of Slip Cast Fused Silica as a Function of the Corrected Firing Time.
Figure 7. Porosity of Slip Cast Fused Silica as a Function of the Corrected Firing Time.
Figure 8. Corrected Time to Reach Minimum Porosity as a Function of Firing Temperature.
Figure 9. Porosity as a Function of Reduced Firing Time.
Firings were made at 2100, 2133, 2166, 2200, and 2300°F for a period of time necessary to enclose the peak strength. Firings at 2000°F were made to 64 hours but were discontinued when extrapolation indicated that approximately 160 hours would be required to reach the peak strength. The modulus of rupture is shown as a function of firing conditions in Figure 10.

The data indicate that the peak strength increases slightly with increasing temperature. While this observation may be true, as a result of the increasing bulk diffusion, there is no statistical difference in the peak strengths and, therefore, no basis for recommending high temperature firing. In addition, the higher temperature firings show much sharper peaks which would make uniform strength development difficult in anything other than small samples. Figure 10 indicates that the practical firing temperature range for slip cast fused silica in an electric kiln is 2100 - 2200°F with the lower temperature being preferable for large castings. Above this temperature range, the peak is so narrow that control would be difficult. At lower temperatures, the peak is sufficiently broad but the required firing times are too long to be practical except for extremely massive castings.

Mention should also be made of the fact that firing in a gas kiln will not follow the same pattern as in an electric kiln. As discussed in Section 8, a high humidity, typical of firing in most gas kilns, produces much more rapid strengthening.

The time at which the peak strength developed was determined from the modulus of rupture data by four point Lagrangian interpolation. These values are tabulated in Table III along with the times to reach the minimum porosity determined in the same manner from the same samples.
Figure 10. Modulus of Rupture as a Function of Firing Conditions.
While the lower temperature peak times are essentially the same for strength and porosity, the higher temperature peak times are appreciably different. The reason for this is apparent. Since silica, like all ceramics, is rather notch sensitive, the formation of internal cracks through thermal shock of the cristobalite will have a marked effect on strength. Even if noticeable bulk diffusion occurs, the cristobalite fracture points act as stress raisers and promote fracture. The porosity, however, would be affected by bulk diffusion equally as well as by cristobalite fracture though, of course, in an opposite direction. As a result, the improved bulk diffusion at the higher firing temperatures would tend to postpone the time of minimum porosity while having far less effect on the time of maximum strength. This would result in the trend shown in Table III. At lower temperature ordinary bulk diffusion would be less rapid and strength and porosity would both react in a similar manner to a given amount of cristobalite fracture, leading to similar peak times.

TABLE III

FIRING TIME TO REACH MAXIMUM STRENGTH
AND MINIMUM POROSITY IN SLIP CAST FUSED SILICA

<table>
<thead>
<tr>
<th>Firing Temperature (°F)</th>
<th>Corrected Time For Maximum Strength (hr.)</th>
<th>Corrected Time For Minimum Porosity (hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2100</td>
<td>49.0</td>
<td>46.7</td>
</tr>
<tr>
<td>2133</td>
<td>19.0</td>
<td>17.4</td>
</tr>
<tr>
<td>2166</td>
<td>8.5</td>
<td>12.4</td>
</tr>
<tr>
<td>2200</td>
<td>3.3</td>
<td>5.7</td>
</tr>
<tr>
<td>2300</td>
<td>1.6</td>
<td>2.0</td>
</tr>
</tbody>
</table>
6. Compressive Strength

Three-quarter-in. diameter by 5-5/8-in. long silica bars were cast in one piece molds using the graphite mold release. Sets of the bars were fired at 2000, 2100, and 2200° F for uncorrected times of 2, 4, 8, and 16 hours and at 2300° F for uncorrected times of 1/2, 1, 2, and 4 hours. The bars were transverse tested, once on a four inch span and twice, using the pieces from the first break, on a two inch span. Following the modulus of rupture determinations, one inch samples were cut from the pieces and crushed on a Tinius-Olsen Super L universal tester at a loading rate of 4,800 pounds per minute. The moduli of rupture, compressive strengths and ratios of the two strengths are tabulated in Table IV.

The compressive strength and modulus of rupture tests differ in their sensitivity to structural flaws. When the silica is fired to a point corresponding roughly to the maximum in the modulus of rupture curve, the cristobalite content in the silica is sufficient to form internal cracks through thermal shock during cooling. Since the axial thermal gradient in the bars is much less than in the radial direction, columnar cracks parallel to the axis tend to develop. The load application in transverse testing is perpendicular to these cracks and will tend to reflect the presence of less extensive cracking. The load application in crushing is parallel to these cracks and the breaking load will not tend to be lowered until much more severe cracking occurs. This behavior causes the maximum in the modulus of rupture curve to appear at a substantially lower time than the maximum compressive strength. This same trend is reflected in the ratio of compressive strength to modulus of rupture which remains relatively constant and low until internal cracking begins. Once this point is passed, however, the ratio increases rapidly.
### TABLE IV

**COMPRESSIVE STRENGTHS AND MODULI OF RUPTURE OF SLIP CAST FUSED SILICA**

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Corrected Firing Time (hr.)</th>
<th>Modulus of Rupture (psi)</th>
<th>Compressive Strength (psi)</th>
<th>Ratio of Compressive Strength to Modulus of Rupture</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>2.23</td>
<td>700</td>
<td>4,580</td>
<td>6.53</td>
</tr>
<tr>
<td>2000</td>
<td>4.23</td>
<td>795</td>
<td>5,210</td>
<td>6.55</td>
</tr>
<tr>
<td>2000</td>
<td>8.23</td>
<td>1,080</td>
<td>6,590</td>
<td>6.10</td>
</tr>
<tr>
<td>2000</td>
<td>16.23</td>
<td>1,460</td>
<td>8,540</td>
<td>5.85</td>
</tr>
<tr>
<td>2100</td>
<td>2.32</td>
<td>1,810</td>
<td>8,960</td>
<td>4.95</td>
</tr>
<tr>
<td>2100</td>
<td>4.32</td>
<td>2,130</td>
<td>11,400</td>
<td>5.35</td>
</tr>
<tr>
<td>2100</td>
<td>8.32</td>
<td>3,310</td>
<td>13,700</td>
<td>4.14</td>
</tr>
<tr>
<td>2100</td>
<td>16.32</td>
<td>4,480</td>
<td>18,300</td>
<td>4.08</td>
</tr>
<tr>
<td>2200</td>
<td>2.38</td>
<td>4,510</td>
<td>20,100</td>
<td>4.46</td>
</tr>
<tr>
<td>2200</td>
<td>4.38</td>
<td>4,760</td>
<td>22,000</td>
<td>4.62</td>
</tr>
<tr>
<td>2200</td>
<td>8.38</td>
<td>4,170</td>
<td>23,100</td>
<td>5.54</td>
</tr>
<tr>
<td>2200</td>
<td>16.38</td>
<td>1,680</td>
<td>20,900</td>
<td>12.44</td>
</tr>
<tr>
<td>2300</td>
<td>1.29</td>
<td>4,520</td>
<td>20,700</td>
<td>4.58</td>
</tr>
<tr>
<td>2300</td>
<td>1.79</td>
<td>4,720</td>
<td>25,800</td>
<td>5.47</td>
</tr>
<tr>
<td>2300</td>
<td>2.79</td>
<td>2,690</td>
<td>20,200</td>
<td>7.51</td>
</tr>
<tr>
<td>2300</td>
<td>4.79</td>
<td>1,970</td>
<td>23,700</td>
<td>12.03</td>
</tr>
</tbody>
</table>
7. Elevated Temperature Tensile Strength

Determinations were begun of the elevated temperature tensile strength of slip cast fused silica using the ring tensile test (P2, P3). Statistical analyses showed that most of the scatter in the tests was due to thermal gradients in the firing chamber. Since reconstruction of the furnace was not feasible, the number of experimental points to be investigated was restricted and the sample size was increased to provide more statistical reliability. Preliminary results of these tests are shown in Figure 11. The firing conditions for the samples are noted on each line. The times are corrected.

8. Effect of Firing Atmosphere

Since many large-scale furnaces are gas fired, extensive use of slip cast fused silica would require knowledge of the effects of high humidity firing atmospheres on the properties of the silica. A survey of the effects of firing atmosphere was made by limited firings in steam, argon, and air (Q1). The properties of the silica under the various firing conditions are shown in Figures 12 through 15.

The results from these tests, while not drawn from large enough sample populations to permit statistical analysis, indicate that steam produces much higher diffusion rates in the silica, leading to earlier strengthening and development of lower porosities. Exclusion of oxygen, as indicated by the argon firings, suppresses diffusion and postpones densification and strengthening.

9. Tracer Permeation System

Reconstruction of the one-sided permeation system was completed (P3)\(^1\). An injection mechanism was devised to permit a reproducible amount of Kr-85 to

\(^1\)Since this method may be new to some readers, a brief summary is given in Appendix A.
Figure 11. Effect of Testing Temperature on the Tensile Strength of Slip Cast Fused Silica processed at Different Firing Temperatures and Times.
Figure 12. Porosity of Slip Cast Fused Silica as a Function of Firing Atmosphere. Firing Temperature, 2200°F.
Figure 13. Bulk Density of Slip Cast Fused Silica as a Function of Firing Atmosphere. Firing Temperature, 2200°F.
Figure 14. Modulus of Rupture of Slip Cast Fused Silica as a Function of Firing Atmosphere. Firing Temperature, 2200°F.
Figure 15. Cristobalite Content of Slip Cast Fused Silica as a Function of Firing Atmosphere. Firing Temperature, 2200°F.
be used in each run. This facilitated the test by eliminating the necessity for completely disassembling the permeation chamber after every run to remove the shattered containment ampoule. Knowledge of the specific activity used remains unnecessary.

Several check runs were made to evaluate the performance of the new system. Three separate runs were made with the same sample. In each run, the sample was removed and replaced on the permeation chamber so that any errors arising from the sample holding technique would be included in the results. The activity curve slopes for the three runs were determined by linear regression using 25 points read from each experimental recorder chart. These values are given with the 95 per cent confidence limits in Table V.

**TABLE V**

ACTIVITY CURVE SLOPES
FOR REPLICATE RUNS

<table>
<thead>
<tr>
<th>Run</th>
<th>Slope</th>
<th>95% Confidence Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-0.204</td>
<td>± 0.001</td>
</tr>
<tr>
<td>B</td>
<td>-0.210</td>
<td>± 0.002</td>
</tr>
<tr>
<td>C</td>
<td>-0.218</td>
<td>± 0.002</td>
</tr>
</tbody>
</table>

Since the effective diffusivity is linearly proportional to the slope, the results of Table V indicate a maximum deviation from the average of the three runs of approximately 3.5 per cent. While the runs are not sufficient for statistical analysis, this reproducibility is encouraging. A second series of runs, large enough to permit statistical analysis, is now underway.

---

Some indication of the validity of the straight line fit of the data is given by the 95 per cent confidence limits on the slopes. If a straight line fit were unjustified, the ranges would be much larger.

Runs were begun to evaluate the influence of firing conditions on the permeability and to determine the effectiveness of flame glazing in sealing the surface of slip cast fused silica.

B. Slip Cast Alumina

Alumina slips were developed using wet milled and dry milled 220 mesh Norton Type 38 Alundum (P3, Q1). Several satisfactory compositions were found with the most suitable slip studied being obtained from 2000 gm. of Alundum, 411 ml. of deionized water, and 23.5 - 25 ml. of concentrated (36 per cent) hydrochloric acid. The mixture was milled for 90 hours at 67 rpm in a one gallon porcelain mill with a ball charge of 4000 gm. of Burundum cylinders. The properties of these slips are summarized in Table VI.

<table>
<thead>
<tr>
<th>TABLE VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PROPERTIES OF ALUMINA SLIP</td>
</tr>
</tbody>
</table>

| Solids Content | 82.1 w/o |
| Specific Gravity | 2.59 |
| Apparent Viscosity* | 2500-2700 cp |
| pH | 3.9-4.1 |

*Brookfield Model LVF Viscosimeter, 30 rpm, Spindle No. 3.
Investigations were made in which the alumina was cast in one piece molds using the graphite mold release. The molds were sealed by gasketed heads, placed under a static, pneumatic, internal pressure, and vibrated on a Syntron vibrating table. The properties of dried 3/4-inch diameter bars, 5-5/8-in. long, are summarized in Table VII.

**TABLE VII**

**PROPERTIES OF ALUMINA BARS SLIP CAST WITH PRESSURE AND VIBRATION**

<table>
<thead>
<tr>
<th>Mold Pressure (psig)</th>
<th>Vibration Amplitude (in)</th>
<th>Casting Time (hr)</th>
<th>Porosity (%)</th>
<th>Bulk Density (gm/cc)</th>
<th>Theoretical Density (gm/cc)</th>
<th>Green Modulus of Rupture (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.010</td>
<td>4.75</td>
<td>32.3</td>
<td>2.54</td>
<td>3.75</td>
<td>1700</td>
</tr>
<tr>
<td>20</td>
<td>0.012</td>
<td>5</td>
<td>31.4</td>
<td>2.57</td>
<td>3.75</td>
<td>1800</td>
</tr>
<tr>
<td>20</td>
<td>0.015</td>
<td>7</td>
<td>30.9</td>
<td>2.59</td>
<td>3.75</td>
<td>1800</td>
</tr>
<tr>
<td>40</td>
<td>0.010</td>
<td>1.75</td>
<td>32.9</td>
<td>2.52</td>
<td>3.75</td>
<td>1500</td>
</tr>
<tr>
<td>40</td>
<td>0.012</td>
<td>2</td>
<td>32.6</td>
<td>2.53</td>
<td>3.75</td>
<td>1600</td>
</tr>
<tr>
<td>40</td>
<td>0.015</td>
<td>4.5</td>
<td>31.2</td>
<td>2.58</td>
<td>3.75</td>
<td>1700</td>
</tr>
<tr>
<td>60</td>
<td>0.010</td>
<td>1.5</td>
<td>32.8</td>
<td>2.52</td>
<td>3.75</td>
<td>1600</td>
</tr>
<tr>
<td>60</td>
<td>0.012</td>
<td>1.75</td>
<td>32.7</td>
<td>2.52</td>
<td>3.74</td>
<td>1600</td>
</tr>
<tr>
<td>60</td>
<td>0.015</td>
<td>2</td>
<td>31.2</td>
<td>2.58</td>
<td>3.75</td>
<td>1700</td>
</tr>
</tbody>
</table>
The vibration served to prevent premature setting of the casting resulting from the thixotropic nature of the slip. This promoted better particle packing and higher cast densities but also increased the casting time. Application of pressure more than offset the increase in casting time, however, and also led to improved mold filling and casting soundness.

Firing surveys were made at a few temperatures without close control. The results of the firing surveys are summarized in Table VIII.

### TABLE VIII

**FIRED PROPERTIES OF SLIP CAST ALUMINA**

<table>
<thead>
<tr>
<th>Firing Temperature (°F)</th>
<th>Firing Time (hr)</th>
<th>Porosity (%)</th>
<th>Bulk Density (gm/cc)</th>
<th>Modulus of Rupture (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2030</td>
<td>8</td>
<td>32.1</td>
<td>2.63</td>
<td>13,800</td>
</tr>
<tr>
<td>2140</td>
<td>8</td>
<td>29.8</td>
<td>2.67</td>
<td>15,800</td>
</tr>
<tr>
<td>2250</td>
<td>8</td>
<td>28.1</td>
<td>2.76</td>
<td>17,000</td>
</tr>
<tr>
<td>3100</td>
<td>2</td>
<td>~ 1.0</td>
<td>~ 3.53</td>
<td>~ 30,000</td>
</tr>
</tbody>
</table>

C. Al-U₃O₈ Interactions

1. Sample Preparation and Testing

The materials used in preparing the pressed compacts were Alcoa No. 140 flake aluminum and Spencer fused U₃O₈. The U₃O₈ was classified into desired particle size cuts by screening in a Syntron sieve shaker following 15 minute milling of 100 gram batches in rubber lined mills. The aluminum powder was not classified prior to use.
Stock mixtures for pressing were prepared in 50 gram batches. The stock powders were produced by blending the components in a small mill for at least eight hours, using an acrylic blade tumbler to assist in mixing. Addition of 1 w/o DuPont Baymal was found to markedly improve powder mixing without otherwise influencing the ignition characteristics. This additive was used in most of the tests.

All tests were carried out using cold pressed pellets 3/8-inch in diameter by about 1/2-inch long with a 1/8-inch diameter by 3/16-inch deep well in one end to permit differential thermal analysis. Each standard pellet was pressed using stock powder mixture blended with 3.2 w/o of water to act as a lubricant. Single step pressing was used with a terminal pressure of 27,000 psi.

The samples were generally subjected to differential thermal analysis (DTA) at a heating rate of 60°F per minute (P2, P3, Q1). The pellets were supported on sealed alumina spaghetti placed over the thermocouples and tested under two atmospheres absolute of argon.

2. Composition Relationships in Al-U<sub>3</sub>O<sub>8</sub> Composites

In evaluating the results of this study with respect to other applications of Al-U<sub>3</sub>O<sub>8</sub> dispersions, knowledge of the relationship between weight per cent and volume per cent is necessary. Since the literature value for the density of U<sub>3</sub>O<sub>8</sub> varies from 7.3<sup>1</sup> to 8.39<sup>2</sup>, an independent measurement appeared in order.

The density of U<sub>3</sub>O<sub>8</sub> was measured in the air displacement system by filling the sample chamber with powder held in place by a polyethylene plug.


The volume of the plug was measured by water immersion. The density measured was 8.11 ± 0.03 gm/cc. A similar measurement was made in a Beckman Air Pycnometer. This determination gave a density of 8.16 ± 0.01 gm/cc.

The calculated relationship between weight and volume per cent is shown in Figure 16.

3. Effect of U₃O₈ Particle Size

A series of DTA tests was run in which the particle size of the U₃O₈ was varied in a 14.6 w/o Al composite (P3). The results are summarized in Table IX.

TABLE IX

EFFECT OF U₃O₈ PARTICLE SIZE ON IGNITION CHARACTERISTICS OF 14.6 w/o Al-U₃O₈ COMPOSITE

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Ignition Temperature (°F)</th>
<th>Peak Height (mv)</th>
<th>Peak Area (mv-sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+100</td>
<td>~ 1950</td>
<td>~ 0</td>
<td>~ 0</td>
</tr>
<tr>
<td>-100 +140</td>
<td>1920</td>
<td>1.48</td>
<td>93</td>
</tr>
<tr>
<td>-140 +200</td>
<td>1860</td>
<td>1.85</td>
<td>130</td>
</tr>
<tr>
<td>-200 +270</td>
<td>1820</td>
<td>2.96</td>
<td>181</td>
</tr>
<tr>
<td>-270 +325</td>
<td>1780</td>
<td>2.18</td>
<td>165</td>
</tr>
<tr>
<td>-325</td>
<td>1790</td>
<td>1.16</td>
<td>118</td>
</tr>
</tbody>
</table>
Figure 16. Conversion Scale for Weight and Volume Per Cent Al in Al-U$_3$O$_8$ Dispersions.
The ignition temperature showed the expected decrease with decreasing particle size. The relative energy yield, indicated by the peak height and peak area, also show the increase to be expected from greater degree of completion of the reaction up to approximately 270 mesh. At particle sizes below 270 mesh, however, this trend failed to continue, presumably because of the poor mixing characteristic of finer powders. This behavior will be the subject of future studies. At first glance, the samples with +100 mesh U₃O₈ might appear not to have reacted. While the DTA test was not sufficiently sensitive to show a reaction clearly, however, electron microprobe analysis did show the results of a reaction as described in Section C-5 of this report.

4. Effect of Composition

Preliminary tests showed a decrease in ignition temperature with increasing aluminum content. Later studies failed to provide satisfactory confirmation of this observation. Part of the difficulty traces to a decrease in sensitivity in DTA tests of higher aluminum content pellets both from an increase in thermal conductivity and a decrease in the amount of reacting U₃O₈ in the constant volume pellet.

In order to define the composition effects more accurately, a study was begun in which pellets of different composition, from approximately six to 65 w/o aluminum, will be heated to 1200, 1400, 1600, and 1800 °F at 60 °F per minute and immediately cooled. Following the heating procedure, the pellets are to be subjected to x-ray analysis. The results from the tests which have been completed are shown in Table X.

Although complete analysis of the results of Table X must await compounding of quantitative standards, a trend seems to be indicated. As the aluminum content increases, an initial incomplete reaction apparently
occurs at or below 1200° F. This corresponds to a small exotherm noted on most of the DTA charts. With increasing aluminum, the reaction appears to become more complete, giving stronger x-ray traces for the UO₂ product. The reaction also appears to continue above 1200° F since the traces for UO₂ seem to become stronger with increasing temperature.

The runs with the 60 w/o composites show a lack of agreement with the other tests. Further runs will be necessary to clarify this point.

TABLE X

<table>
<thead>
<tr>
<th>Maximum Temperature (°F)</th>
<th>Aluminum Content (w/o)</th>
<th>Al₂O₃</th>
<th>UO₂</th>
<th>UAl₂</th>
<th>UAl₃</th>
<th>UAl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>6.3</td>
<td>N</td>
<td>NW</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>1200</td>
<td>26.6</td>
<td>N</td>
<td>W</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>1200</td>
<td>31.5</td>
<td>N</td>
<td>WM</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>1200</td>
<td>35.7</td>
<td>N</td>
<td>M</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>1200</td>
<td>60.0</td>
<td>S</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>S</td>
</tr>
<tr>
<td>1200</td>
<td>65.0</td>
<td>N</td>
<td>MS</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>1300</td>
<td>65.0</td>
<td>N</td>
<td>S</td>
<td>N</td>
<td>W</td>
<td>N</td>
</tr>
<tr>
<td>1400</td>
<td>6.3</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>1400</td>
<td>26.6</td>
<td>N</td>
<td>M</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>1400</td>
<td>31.5</td>
<td>N</td>
<td>M</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>1400</td>
<td>35.7</td>
<td>N</td>
<td>MS</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>1400</td>
<td>65.0</td>
<td>N</td>
<td>S</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>1900</td>
<td>60.0</td>
<td>M</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>M</td>
</tr>
</tbody>
</table>

*N = None
W = Weak
M = Medium
S = Strong
NW = None to weak
WM = Weak to medium
MS = Medium to Strong
5. Microprobe Analysis

Fired samples of a 14.6 w/o Al composite were subjected to commercial electron microprobe analysis.\(^1\) The pellets were found to contain α-Al\(_2\)O\(_3\), UO\(_2\), and UAl\(_2\). Although x-ray analysis indicated the presence of UAl\(_3\), no confirming indications were found upon microprobe analysis. This implies that the UAl\(_3\) must be present as thin veins, probably surrounding the UAl\(_2\) particles.

Micrographs of the microprobed samples are shown in Figure 17.

6. Thermochemical Calculations

Four potential "terminal" reactions have been indicated by the results of this study:

\[
\begin{align*}
\text{U}_3\text{O}_8 + \text{Al} &\rightarrow \frac{2}{3} \text{Al}_2\text{O}_3 + 3\text{UO}_2 \quad (4.1 \text{ w/o}) \quad (3) \\
\text{U}_3\text{O}_8 + \frac{3}{8} \text{Al} &\rightarrow \frac{8}{3} \text{Al}_2\text{O}_3 + 3\text{UAl}_2 \quad (26.6 \text{ w/o}) \quad (4) \\
\text{U}_3\text{O}_8 + \frac{4}{3} \text{Al} &\rightarrow \frac{8}{3} \text{Al}_2\text{O}_3 + 3\text{UAl}_3 \quad (31.5 \text{ w/o}) \quad (5) \\
\text{U}_3\text{O}_8 + \frac{5}{2} \text{Al} &\rightarrow \frac{8}{3} \text{Al}_2\text{O}_3 + 3\text{UAl}_4 \quad (35.7 \text{ w/o}) \quad (6)
\end{align*}
\]

In practice, most composites react by a combination of at least two of the above mechanisms. For aluminum contents from 4.1 to 35.7 w/o, reactions involving two of the above mechanisms and complete reaction of the U\(_3\)O\(_8\) have one degree of freedom. For a 14.6 w/o aluminum compact, for instance, x-ray diffraction indicates complete reaction with the formation of some UAl\(_2\) and some UAl\(_3\). The general reaction is thus (Q1)

---

\(^1\)Advanced Metals Research, Somerville, Massachusetts.

\(^2\)Figures in parentheses are the weight percentages of aluminum required for the particular reaction to go to completion.
Figure 17. Microstructure of 14.6 w/o Al-U₃O₈ Composite with +100 Mesh U₃O₈.
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\[ \frac{16}{3} \text{Al} + U_{3}O_{8} = 3xUO_{2} + \left( \frac{8}{3} - 2x \right) Al_{2}O_{3} + (9 - 13x) UAl_{2} + (10x - 6) UAl_{3} \quad (7) \]

by a material balance where

\[ x = \frac{U_{3}O_{8} \rightarrow UO_{2}}{\text{mole } U_{3}O_{8} \text{ originally present}}. \]

The actual reaction representing a particular compact will then be between the two terminal reactions

\[ \frac{16}{3} \text{Al} + U_{3}O_{8} = 1.8 UO_{2} + 1.467 Al_{2}O_{3} + 1.2 UAl_{2} \quad (8) \]

and

\[ \frac{16}{3} \text{Al} + U_{3}O_{8} = 2.076 UO_{2} + 1.283 Al_{2}O_{3} + 0.923 UAl_{3}. \quad (9) \]

The corresponding energy balances are

\[ (\Delta H_R)_{\text{max}} = 1.8 \Delta H_{\text{fUO}_2} + 1.467 \Delta H_{\text{fAl}_2O_3} + 1.2 \Delta H_{\text{fUAl}_2} - \Delta H_{\text{fU}_3O_8} \quad (10) \]

and

\[ (\Delta H_R)_{\text{min}} = 2.076 \Delta H_{\text{fUO}_2} + 1.283 \Delta H_{\text{fAl}_2O_3} + 0.923 \Delta H_{\text{fUAl}_2} - \Delta H_{\text{fU}_3O_8} \quad (11) \]

Equations 10 and 11 are the limits on the maximum credible energy release for 14.6 w/o aluminum composites. In order to permit calculation of this energy release, estimates were made of the heats of formation of the uranium-aluminum intermetallic compounds (Q\(I\)). These values and the heats of formation of the uranium and aluminum oxides\(^1\) are tabulated in Table XI.

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>U₃O₈</th>
<th>UO₂</th>
<th>UA₁₂</th>
<th>UA₁₃</th>
<th>UA₁₄</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.2</td>
<td>853.5</td>
<td>259.2</td>
<td>22.3</td>
<td>25.2</td>
<td>31.2</td>
<td>399.6</td>
</tr>
<tr>
<td>400</td>
<td>852.6</td>
<td>258.9</td>
<td>22.4</td>
<td>25.3</td>
<td>31.3</td>
<td>399.7</td>
</tr>
<tr>
<td>500</td>
<td>851.7</td>
<td>258.6</td>
<td>22.7</td>
<td>25.6</td>
<td>31.6</td>
<td>399.6</td>
</tr>
<tr>
<td>600</td>
<td>850.7</td>
<td>258.3</td>
<td>23.2</td>
<td>26.2</td>
<td>32.3</td>
<td>399.5</td>
</tr>
<tr>
<td>700</td>
<td>849.9</td>
<td>258.0</td>
<td>23.9</td>
<td>27.0</td>
<td>33.2</td>
<td>399.2</td>
</tr>
<tr>
<td>800</td>
<td>849.2</td>
<td>257.8</td>
<td>24.9</td>
<td>28.1</td>
<td>34.4</td>
<td>399.1</td>
</tr>
<tr>
<td>900</td>
<td>848.8</td>
<td>257.6</td>
<td>26.1</td>
<td>29.4</td>
<td>35.9</td>
<td>398.9</td>
</tr>
<tr>
<td>935</td>
<td>848.6</td>
<td>257.6</td>
<td>26.6</td>
<td>30.0</td>
<td>36.5</td>
<td>398.8*</td>
</tr>
<tr>
<td>935</td>
<td>850.7</td>
<td>258.3</td>
<td>32.3</td>
<td>38.2</td>
<td>47.2</td>
<td>403.9*</td>
</tr>
<tr>
<td>1000</td>
<td>850.3</td>
<td>258.2</td>
<td>32.7</td>
<td>38.7</td>
<td>47.7</td>
<td>403.7</td>
</tr>
<tr>
<td>1045</td>
<td>850.1</td>
<td>258.1</td>
<td>33.0</td>
<td>39.0</td>
<td>48.1</td>
<td>403.6</td>
</tr>
<tr>
<td>1045</td>
<td>853.5</td>
<td>259.2</td>
<td>34.1</td>
<td>40.1</td>
<td>49.2</td>
<td>403.6</td>
</tr>
<tr>
<td>1100</td>
<td>853.0</td>
<td>259.1</td>
<td>34.4</td>
<td>40.5</td>
<td>49.6</td>
<td>403.4</td>
</tr>
<tr>
<td>1200</td>
<td>852.0</td>
<td>258.8</td>
<td>34.9</td>
<td>41.1</td>
<td>50.4</td>
<td>403.0</td>
</tr>
<tr>
<td>1300</td>
<td>851.0</td>
<td>258.4</td>
<td>35.5</td>
<td>41.7</td>
<td>51.1</td>
<td>402.6</td>
</tr>
<tr>
<td>1400</td>
<td>850.0</td>
<td>258.1</td>
<td>36.0</td>
<td>42.3</td>
<td>51.8</td>
<td>402.3</td>
</tr>
</tbody>
</table>

*These values are actually for 931.7 °K. In view of the small difference from 931.7 to 935, however, they are used in all calculations in this report as 935 °K values (Q1).
The values of Table XI were used to calculate the energy release corresponding to Equations 10 and 11. The results are plotted in Figure 18.

At 35.7 w/o Al, the material balance describing the maximum credible energy release is determinate. The isothermal energy release is shown in Figure 19 as a function of ignition temperature.

Since the maximum credible energy release does not vary rapidly with a change in ignition temperature, calculation of an approximate maximum energy yield as a function of composition is not too misleading. Since this information is most likely to be of interest in reactor calculations, the energy release is shown in Mw-sec per kg of fuel in Figure 20. In all cases, the material balance assumed is that productive of the greatest energy evolution and complete reaction is postulated. Since the reaction in compacts containing more than 35.7 w/o Al cannot consume all the aluminum present, the maximum credible energy release becomes constant in terms of a unit quantity of U₃O₈ reacting. Per unit mass of fuel, however, the excess aluminum dilutes the reacting U₃O₈ and the specific energy evolution decreases.

7. Photographic Studies

Attempts were continued to follow the Al-U₃O₈ reaction visually. Telephoto motion pictures and still photographs were made of several pellets igniting in air. While these initial attempts involved largely uncontrolled heating rates, the results were very interesting.

Figure 21 shows a single exposure and a film strip of a 14.6 w/o Al thermet igniting. Since the rear of the pellet was heated fastest in the test during which the motion picture was made, ignition began at that point in the second frame of the film strip. The ignition spread rapidly, enveloping
Figure 18. Limiting Energy Yields from Al-U$_3$O$_8$ Thermet of 14.6 w/o Al.
Figure 19. Maximum Energy Yield from Al-U₃O₈ Thermet of 35.7 w/o Al.
Figure 20. Approximate Maximum Credible Energy Release from Al-U₃O₈ Fuel.
Figure 21. Photographs of Al-U$_3$O$_8$ Thermet Igniting.
the pellet by the fourth frame, a time interval of approximately 0.1 sec. Some idea of the violence of the reaction is given by the enlarged single exposure from a similar test.

D. Be-U₃O₈ Interactions

Studies were resumed with the Be-U₃O₈ thermets. The first composition studied contained 7.9 w/o of -325 mesh beryllium compounded in the same manner as the Al-U₃O₈ thermets. These samples showed sharp ignition peaks on DTA at 1820° F. The peak height was about double that typical of the Al-U₃O₈ thermet and the peak area was almost twice as great. These preliminary results indicate that the Be-U₃O₈ reaction may be more energetic than the Al-U₃O₈ reaction.

No indications were obtained of a lower temperature reaction in the Be-U₃O₈ composites similar to that seen in the Al-U₃O₈ composites.
IV. DISCUSSION

The fabrication procedure to be recommended for slip cast fused silica has been clarified somewhat during the past year. For most engineering applications, use of any of the three plasters tested, and probably any common pottery plaster, appears satisfactory. Although there are clear differences in the surface devitrification rates of samples cast in different plasters, these differences are not reflected in overt changes in fired strength. In more critical applications, preferential use of U. S. Gypsum Puritan plaster should be considered in view of its low devitrification promotion.

In most applications, use of either Keltec or graphite as a mold release should prove satisfactory. Keltec would normally be preferable in simple molds since it gives some support to the green casting. In more complex molds, particularly those with deep, close draws, the better release characteristics of graphite would favor its use. In all cases, a mold release must be used in order to prevent acceleration of devitrification by calcium leached from the mold. Of even more critical importance is removal, before firing, of the Keltec film from any casting employing it as a mold release. If the Keltec remains in place during firing, the devitrification rate will exceed that resulting from failure to use a mold release at all.

The modulus of rupture firing profile continues to be very reminiscent of age hardening curves in metals. The optimum firing condition for maximum strengthening appears to be 2200° F for four hours. This pertains only to firing in electric kilns, however. The study of steam fired silica indicates quite clearly that firing in a gas-fired furnace, with the higher concomitant humidity, would accelerate the strengthening process substantially. Four hours
at 2200° F in a gas fired kiln would undoubtedly produce badly overfired castings. Preliminary results do indicate, however, that lower temperature steam firing may be quite advantageous in the production of greater strength and lower porosity.

Users of slip cast fused silica should also keep in mind the fact that the 2200° F for four hour firing is applicable only to moderate sized castings. In large castings, the low thermal conductivity of the silica could result in underfired cores and non-uniform properties. In such a case, lower temperature firing would be preferable, for instance 2130° F for 16 hours.

The air displacement porosity system proved to be quite accurate and versatile. Such a system permits testing of materials which cannot be immersed in liquids for normal porosity measurement. Unfired compacts and bulk powders can thus be studied when testing by water immersion would be impossible. The system appears to be amenable to automation for quality control use. The porosity measurements made using air displacement give a much more accurate index of the true void fraction than those from a water displacement technique. All in all, the air displacement method appears eminently worth of extensive development and use.

The comparison of the modulus of rupture and crushing strength tests showed clearly the difference between uni- and multi-directional stressing in notch sensitive materials. The compression test of slip cast fused silica tends to load the sample along the axis of the structural flaws, causing them to act as voids rather than as stress concentrators. The modulus of rupture causes stressing in at least two directions, however, so that the internal flaws do act as stress raisers. A small amount of cracking in slip cast fused silica will thus be reflected sooner in the modulus of rupture than in the compression
strength, resulting in a more sensitive test. The modulus of rupture is thus more satisfactory as a strength index for slip cast fused silica either for design purposes or for investigations of fabrication parameters.

The substantial improvement in properties of slip cast alumina afforded by pressure application and mold vibration recommend similar studies with slip cast fused silica. Since the silica slip shows little tendency toward bridging during casting, mold vibration would be expected to have less effect than with the alumina. Pressure application, on the other hand, would offer significant advantages in that faster casting would improve the economics of the fabrication process and should give more uniform casting through control of slip sedimentation.

Some comment is necessary concerning the Al-U₃O₈ investigation, particularly with respect to application of these results to hazards evaluation of Al-U₃O₈ dispersion fuels. At all times, the nature of the reacted Al-U₃O₈ system must be kept in mind. Since the reacted mixture contains UAl₂, UA1₃, and UA1₄, the determination of the energy release spectrum is not independent of the thermal kinetics of the environment. Upon ignition, for instance, solid UAl₂, UA1₃, UO₂, and Al₂O₃ should first form since the ignition temperature is below the melting points of these products. A considerable amount of the energy evolved by the Al-U₃O₈ reaction will be absorbed in melting these products in an adiabatic situation. This will tend to limit the maximum adiabatic temperature rise. In addition, if melting of the products does occur in a practical case, the energy released by the Al-U₃O₈ reaction will be released to the reactor in two or more bursts. The first will correspond to sensible heat removed during the primary ignition. The subsequent bursts will not occur until the reactants are cooled through their melting points. In some cases, the cooling could be so
rapid that the decomposed intermetallics would be quenched in rather than recombining. This would be an entirely possible occurrence with UAl₁₄. In a 35.7 w/o Al dispersion, the composition required for complete formation of UAl₁₄, this alone would reduce the maximum energy yield from about 1.84 Mw-sec/Kg U₃O₈ to about 1.7 Mw-sec/Kg U₃O₈, a substantial change.

Evidently, then, data which will allow interpretation of the Al-U₃O₈ reaction either as a fabrication process or as a reactor hazard must include both kinetic and thermodynamic considerations. It is hoped that a combination thermal history and calorimetric evaluation of igniting Al-U₃O₈ mixtures may be obtained in the future report periods.

The confirmation of a lower temperature short-time reaction in Al-U₃O₈ composites also introduces new topics for consideration. Since some UO₂ has been found by 1400° F in most composites in the practical fuel composition range, it appears likely that the energy release may not occur in any case as a one burst yield. This, in addition to the factors discussed above, could limit the effects of an Al-U₃O₈ interaction. At the same time, the existence of UO₂ prior to the violent ignition, at least in the lower aluminum content composites where the reaction is complete, indicates a desirability for further search for possible Al-UO₂ reactions.
V. PERSONNEL

The work discussed in this report was conducted in the Ceramics Branch, Mr. J. D. Walton, Head. The project was directed by Dr. J. D. Fleming with Mr. J. W. Johnson acting as Assistant Project Director. Major contributing personnel were:

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- Mr. A. R. Colcord, Group Leader
- Dr. R. F. Hochman, Research Assistant
- Mr. J. N. Harris, Assistant Research Engineer
- Mr. N. K. Hearn, Assistant Research Physicist
- Mr. C. E. Burnett, Technician
- Mr. R. K. Butz, Technician
- Mr. P. A. Darius, Technician
- Mr. B. C. Diesen, Technician
- Mr. A. C. Evans, Technician
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Senior Investigator

J. W. Johnson
Assistant Project Director

J. D. Walton, Head
Ceramics Branch

F. Bellinger, Chief
Material Sciences Division
VI. APPENDICES
APPENDIX A

Tracer Permeation System

The Kr-85 tracer permeation system consists of a glass chamber with an opening across which a silica test disc is clamped and an aluminum window through which a geiger counter detects activity in the chamber. At a particular time, a small amount of Kr-85, approximately 0.5 mc., is injected into the system. As it diffuses through the test disc, a continuous record of the chamber activity is made. The activity is proportional to the Kr-85 concentration and may be used to calculate a permeability or effective diffusivity.

An unsteady state analysis (P2) indicated that the concentration gradient of the Kr-85 in the sample being tested should approach linearity at a rate which would greatly exceed the rate of hot side activity change. Under these circumstances, the concentration should be very nearly a linear function of position at all times. As a result,

\[
\frac{dC}{dx} = K_1
\]  \hspace{1cm} \text{(11)}

where

- \( C \) = krypton concentration
- \( x \) = position in sample measured from cold side
- \( K_1 \) = constant

At any time, Equation 11 may be integrated to give

\[
C = K_1 x + K_2
\]  \hspace{1cm} \text{(12)}
with the boundary conditions

\[ C(x = 0) = 0 \]
\[ C(x = L) = C_H \]

where

\[ C_H = \text{hot side concentration at the time of interest} \]
\[ L = \text{sample thickness} \]

Substitution of the boundary conditions gives

\[ K_\perp = \frac{C_H}{L} \]  \hspace{1cm} (13) \]

Substitution of Equation 13 into Equation 11 gives

\[ \frac{dC}{dx} = \frac{C_H}{L} \]  \hspace{1cm} (14) \]

Since the system shows such a rapid approach to equilibrium, the steady state diffusion equation applies, in which

\[ G = -DA \frac{dC}{dx} \]  \hspace{1cm} (15) \]

where

\[ G = \text{permeation rate of tracer gas} \]
\[ D = \text{effective diffusivity} \]
\[ A = \text{sample area perpendicular to permeation path} \]

Substitution of Equation 14 into Equation 15 gives

\[ G = -\frac{D \cdot A \cdot C_H}{L} \]  \hspace{1cm} (16) \]
Since

\[ G = \frac{dn_H}{d\theta} \quad 17 \]

where

\[ n_H = \text{moles of tracer gas in hot cross} \]
\[ \theta = \text{time}, \]

Equation 16 may be written

\[ \frac{dn_H}{d\theta} = - \frac{DAC_H}{L}. \quad 18 \]

The hot side concentration is expressed by

\[ C_H = \frac{n_H}{V} \quad 19 \]

where

\[ V = \text{volume of Pyrex cross} \]

Equation 18 becomes

\[ \frac{dn_H}{d\theta} = - \frac{DAn_H}{LV} \quad 20 \]

The tracer gas activity in the cross is directly proportional to the number of tracer gas molecules in the cross, so that

\[ a_H = K_3n_H \quad 21 \]

where
\( a_H = \text{hot side activity} \)

\( K_3 = \text{constant.} \)

Also, from Equation 21,

\[
\frac{da_H}{d\theta} = K_3 \frac{dn_H}{n_H}. \tag{22}
\]

Substitution of Equations 21 and 22 into Equation 20 gives

\[
\frac{da_H}{d\theta} = -\frac{DAa_H}{LV}. \tag{23}
\]

Separation of the variables and integration of Equation 23 gives

\[
\ln a_H = -\frac{DA}{LV} \theta + K_4. \tag{24}
\]

with the boundary condition

\[
a_H (\theta = 0) = a_H^0
\]

where

\( a_H^0 = \text{original hot side activity.} \)

Substitution of the boundary condition gives

\[
\ln a_H = \ln a_H^0 - \frac{DA}{LV} \theta. \tag{25}
\]

Equation 25 indicates that a semilog plot of the hot side activity as a function of time should yield a straight line of slope \( -\frac{DA}{LV} \). Since \( A, L, \) and \( V \) are known, the effective diffusivity can be calculated.
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PROJECT NO. B-153

MATERIALS FOR HIGH TEMPERATURE NUCLEAR ENGINEERING APPLICATIONS

By J. D. Fleming, J. W. Johnson,

Paul Boland, and S. E. Bomar

Prepared for
U. S. Atomic Energy Commission
Oak Ridge, Operations Office
Oak Ridge, Tennessee

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1 June

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia
FOREWORD

The investigation reported in this document was performed by the Engineering Experiment Station of the Georgia Institute of Technology under U. S. Atomic Energy Commission Contract No. AT-(40-1)-2483. The work was sponsored by the Division of Reactor Development, Fuels and Materials Development Branch, Mr. J. M. Simmons, Chief. The contract was administered by the Oak Ridge Operations Office, Reactor Division, Dr. David F. Cope, Director.

This report covers the period from July 1, 1962 to June 1, 1963.
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This report contains 65 pages.
I. INTRODUCTION

The excellent thermal shock resistance and indications of good radiation resistance of fused silica have recommended it for consideration for use in high temperature radiation fields. With the development at Georgia Tech of techniques for economical fabrication of large and complex silica shapes by slip casting, major objections to this material, on the basis of cost and fabrication difficulty, have been overcome.

Since fused silica has not, until recently, been considered an engineering material, many gaps exist in the data necessary for its evaluation for use in reactors. One object of Project B-153 is the determination and compilation of sufficient data for this evaluation and for systems design based on slip cast fused silica.

Slip casting offers several advantages as a fabrication technique for refractory materials. In many cases, the materials may be formed with a degree of purity and structural isotropy not obtainable with other methods of fabrication. Equally as important, the low capital investment required for slip casting is particularly attractive in the nuclear energy field where many "one of a kind" components must be fabricated. A second object of Project B-153 is the development of techniques for slip casting a wide variety of refractory materials. In addition to fused silica, investigations are currently being made of slip cast alumina.

The competitiveness of nuclear power systems depends strongly on the extent to which use can be made of potentially high operating temperatures. The fuels required to operate stably at these high temperatures must be fabricated at equally high temperatures if conventional fabrication techniques are used. The fabrication problems and expense increase with fabrication temperature in more than linear proportion, adversely affecting the economics of the system.
Project B-153 also is concerned with an investigation of a novel process in which the material being fabricated furnishes the high fabrication temperatures required. This process consists of selecting materials which will undergo highly exothermic chemical reactions, producing both high temperatures and desirable reaction products. To date, aluminum and beryllium reduction of oxides of uranium has been studied, with the major emphasis being placed on aluminum reduction of $\text{U}_3\text{O}_8$. Since $\text{Al}-\text{U}_3\text{O}_8$ dispersions are in common use as reactor fuels, the results of this study are obviously of interest in hazards evaluation. Several special studies of $\text{Al}-\text{U}_3\text{O}_8$ dispersions are included in the program to assist hazards evaluation.
II. SUMMARY

The compressive strength of slip cast fused silica was determined as a function of firing conditions under air at one atmosphere absolute. The maximum compressive strength of 29,000 psi was reached after firing at 2300°F for three hours. The compressive strength did not decrease sharply on overfiring. At 2200°F, the compressive strength peaked at 23,000 psi after eight hours but only fell to 21,000 psi after overfiring to 16 hours.

Studies were made of the strengthening and bulk densification kinetics of slip cast fused silica fired in air at one atmosphere absolute and in steam at one and two atmospheres absolute. Strengthening contours were established for all three firing atmospheres. Steam proved effective in promoting more rapid strengthening and strengthening to a higher level. For firing at 2100°F, the maximum moduli of rupture were reached in approximately 48 hours in one atmosphere air, 10 hours in one atmosphere steam, and 5.2 hours in two atmosphere steam. The maximum moduli of rupture in the three atmospheres were, respectively, 4200 psi, 4600 psi, and 6200 psi.

Bulk properties of silica fired in air and in steam were determined by air displacement. While the porosity reached a minimum and began a secondary increase in air firing, the porosity in steam firing decreased continuously over the firing range studied. The minimum porosity attained in air firing was approximately 14 per cent. In the most extended firings in one and two atmosphere steam, the porosity fell to approximately 11.2 and 11.0 per cent, respectively. Even under these conditions, no indication was given that the porosity might be reaching a minimum.

Sintering, as indicated by porosity, was much more rapid in steam than in air. At 2100°F, for example, a porosity of 15 per cent was reached after 20 hours in one atmosphere air, seven hours in one atmosphere steam, and four hours in two atmosphere steam.
Although the initial bulk densification rate was higher in one atmosphere air than in one atmosphere steam, a higher average rate was maintained in one atmosphere steam. A uniformly higher rate was obtained in two atmosphere steam than in one atmosphere air. The times required to reach 1.90 gm per cc. bulk density in firing at 2100°F were 9.3 hours for one atmosphere air, 8.7 hours for one atmosphere steam, and four hours for two atmosphere steam. The bulk densification rate in air showed a continuous decrease with increasing firing time. In steam, the bulk densification rate was essentially constant up to the time of maximum strengthening. At this point an abrupt decrease occurred in the densification rate. This was tentatively attributed to blockage of viscous flow at the particle surfaces by completion of a continuous devitrified layer on the particle surfaces. This effect would be masked in air firing where the probable sintering mechanism is plastic, rather than viscous, flow.

Methods were developed for the determination of several activation energies characterizing transport processes in the firing of slip cast fused silica. For early sintering, the activation energies were 69 kcal per mole in air and 110-120 in steam; for maximum strengthening, 205 in air and 90 in steam; and for devitrification, 98 in steam.

Analysis of the early devitrification process during firing of slip cast fused silica indicated that the cristobalite content should vary with the cube of firing time. Both preliminary air and one atmosphere steam data were correlated fairly well by this criterion. Extrapolation of the data plots to zero firing time indicated, in both cases, that the slip initially contains approximately 0.5 per cent cristobalite.

A study was made of the influences of pressure application and mold vibration on casting of fused silica slip. Application of 20 psig pressure
to the casting slip decreased the time for casting a 3/4-in. diameter bar from 150 minutes to 33 minutes. Further pressure increase to 60 psig decreased the casting time linearly to 17 minutes. The casting time was not noticeably affected by mold vibration. The application of pressure during casting resulted in an increase in cast porosity. The cast porosity was decreased by mold vibration, but the porosity decrease from axial mold vibration at the maximum amplitude of 0.015-in. was unable to offset the increase from pressure application above 20 psig. The dry modulus of rupture was decreased by pressure application and increased by mold vibration. At the maximum vibration amplitude, in the absence of pressure application, the modulus of rupture was increased from 160 psi to 217 psi. Application of pressure in excess of 20 psig returned the modulus of rupture to 160 psi even with maximum vibration.

A statistical study was made of the effects of 0.1 and 1 w/o additions of Baymal on the reaction characteristics of Al-85.4 w/o U₃O₈ composites. No statistical indication was obtained of an influence of 0.1 w/o Baymal additions on the ignition characteristics of the pellets. Addition of 1 w/o Baymal showed a significant decrease in the ignition temperature, peak height and peak area in differential thermal analysis at greater than the 95 per cent confidence level.

The effects of U₃O₈ particle size were studied in Al-75 w/o U₃O₈ composites. Only the -325 mesh U₃O₈ showed significantly different ignition characteristics, yielding decreased ignition temperatures and increased differential thermal analysis peak areas.

One differential thermal analysis furnace was converted to chromel-alumel thermocouples to give increased sensitivity. Al-50 w/o U₃O₈ composites were
pressed using "dead-burned" Y-12 U₃O₈ supplied by ORNL. Differential thermal analysis was applied to these pellets using various standards. Although all standards displayed the aluminum melting endotherm and high temperature reaction exotherm, only a pre-fired Al-U₃O₈ pellet or graphite gave reasonably satisfactory curves. These two standards gave very similar results with the principal difference being that the excess aluminum in the pre-fired Al-U₃O₈ standard partially offset the aluminum melting endotherm of the unknown.

Investigations were begun to determine the feasibility of measuring the aluminum conversion and reaction energy by differential thermal analysis of reacting Al-U₃O₈ composites. Although trends were observed, quantitative comparisons were not possible due to complications, probably arising from uranium oxide stoichiometry changes, in the x-ray diffraction analysis. Application of the DTA technique to calorimetry of reacting Al-U₃O₈ composites appears promising although only two samples have been run.

Metallographic examination of fired ATR specimens was begun. Relief polishing provided at least partial delineation of the structures present. Attempts were begun to identify the microconstituents by microhardness testing and electron microprobe analysis.

Rough determinations were made of the load-bearing capability of ATR composites at elevated temperatures. A supported 1/4-in. diameter circular area in a 90 mil thick specimen sagged under approximately one psi pressure differential at temperatures of 1350 and 1700°F. Reacted specimens did not sag under 4 psi differential, the maximum attainable in the apparatus, at 1860°F. Metallographic examination of the sagged specimens indicated that the pressure differential caused aluminum to exude from the sample surface, leaving the oxide behind. This implies that a continuous network, possibly of Al₂O₃, exists in the rolled ATR dispersion. Failure appeared to occur
only after considerable aluminum exudation permitted the oxide network to collapse.

A high temperature x-ray diffraction system was constructed to permit investigation of Al-U$_3$O$_8$ reaction kinetics. The system performed well during trials but difficulties arose when the test runs were begun. The counting tube became inoperative and an adapter had to be machined to fit the new tube to the system. After this was done and the study was resumed, bloating began occurring in the compacts during testing. The bloated specimens blocked the x-ray diffraction beam, preventing diffraction analysis. The source of this bloating has not yet been determined. A delay of approximately a month has already resulted from these difficulties.

Initial studies were made to compare reactions in cold pressed Al-UO$_2$ pellets with those in cold pressed Al-U$_3$O$_8$ pellets. Differential thermal analysis curves from the two systems were quite similar in appearance. The reaction exotherm in Al-UO$_2$ occurred at 1820°F compared with 1780°F for Al-U$_3$O$_8$. The energy evolution kinetics appeared more rapid in Al-UO$_2$ although insufficient samples were tested to permit statistical comparison.
III. EXPERIMENTAL PROGRESS AND DISCUSSION

A. Slip Cast Fused Silica

1. Compressive Strength

Compression testing of the slip cast fused silica was completed. Samples were fired at temperatures of 2000, 2100, 2133, 2166, 2200, and 2300°F for times sufficient to enclose the peak strength in all cases except the 2000°F firings. Sections 1-inch long were diamond sawed from 3/4-inch diameter by 5-5/8-inch long bars and crushed in a Tinius Olsen Super L universal tester. A spherical bearing block was used in the tests, and the ends of the bars were cushioned with 0.048-inch thick cardboard to prevent edge chipping. A loading rate of 4800 pounds per minute was used throughout since the compressive strength was statistically independent of loading rate.

The compressive strength of slip cast fused silica is shown as a function of firing condition in Figure 1. The curves are quite similar in shape to the modulus of rupture profiles determined previously. The positions of the maxima differed from the peak positions in the modulus of rupture and porosity curves. A comparison of these peak positions, determined by four point Lagrangian interpolation, is given in Table I.

The differences in the three firing properties are related to differing structure dependence. Any internal cracking will normally be in an axial orientation since the radial thermal gradient will be much higher than the axial gradient during cooling. These axial cracks would act as stress raisers and lower the modulus of rupture perpendicular to the cracks long before the compressive strength, parallel to the cracks, would be affected and before the cracking would be extensive enough to show a secondary porosity increase. Also,

the cracking might well be reflected in a higher porosity before becoming sufficiently extensive to influence the strength parallel to the cracks. These observations would imply that the modulus of rupture, porosity, and compressive strength should peak in that order with increasing time and that the differences in peak time should increase with increasing firing temperature as a result of the increased radial thermal gradient. This expectation is supported moderately well by the data of Table I.

**TABLE I**

FIRING TIMES FOR MAXIMUM MODULUS OF RUPTURE AND COMpressive STRENGTH AND MINIMUM POROSITY IN SLIP CAST FUSED SILICA

<table>
<thead>
<tr>
<th>Firing Temperature (°F)</th>
<th>Firing Time for Maximum Modulus of Rupture (hr)</th>
<th>Firing Time for Maximum Compressive Strength (hr)</th>
<th>Firing Time for Minimum Porosity (hr)</th>
</tr>
</thead>
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<tr>
<td>2100</td>
<td>49.0</td>
<td>47.4</td>
<td>46.7</td>
</tr>
<tr>
<td>2133</td>
<td>19.0</td>
<td>13.8</td>
<td>17.4</td>
</tr>
<tr>
<td>2166</td>
<td>8.5</td>
<td>10.0</td>
<td>12.4</td>
</tr>
<tr>
<td>2200</td>
<td>3.3</td>
<td>8.0</td>
<td>5.7</td>
</tr>
<tr>
<td>2300</td>
<td>1.6</td>
<td>3.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Figure 1. Compressive Strength of Slip Cast Fused Silica Fired Under One Atmosphere of Air.
2. Effects of Firing Conditions
   
a. Conditions Studied:

   The sintering behavior of slip cast fused silica was studied in firing atmospheres of air and steam. All bars were cast in one piece cylindrical molds using the graphite mold release.
   
   Air firings were made in a bottom loading kiln with the air static and at ambient pressure and humidity. Firings were made at 2000, 2100, 2133, 2166, 2200, and 2300°F. The firing was timed from the instant the bars were inserted into the preheated furnace. Firings were made over a time range sufficient to enclose the peak strength. At least two sets of bars, and usually three, were fired at each point.

   Steam firings were made in a tube furnace. Water was fed directly to the furnace from a ballast tank with air in the vapor space held at a constant pressure by a compressed air regulator. The water flow was adjusted with a rotameter to a flow rate of 0.72 pounds per hour. The following firing procedure was used:

   a) The furnace was preheated to the desired firing temperature.
   
   b) A set of 11 test bars was placed in the center of the heating tube.
   
   c) The tube was closed and evacuated.
   
   d) The tube was backfilled with argon, and a vacuum was drawn. This step was repeated four times.
   
   e) When the furnace again reached the preheat level, water was introduced to the furnace at the rate of 0.72 pounds per hour.
   
   f) Taking zero time to be the instant water was first introduced to the furnace, the bars were fired over the desired time span.

1. Firings under air in the tube furnace gave results not significantly different from firings in the bottom loading kiln.
g) During firing, the steam pressure was maintained at the desired level by a low pressure drop direct vent to the atmosphere for the one atmosphere firings and by a 15 psig pop-off vent valve for the two atmosphere firings. Steam firings were made at 2000, 2100, and 2200°F for times sufficient to enclose the maximum strength. Duplicate or triplicate firings were made at all points except the longest firing times at 2000°F.

b. Effects of Firing Conditions on Strength:

The modulus of rupture of each of the fired bars was determined in three point loading on a Tinius-Olsen Super L universal tester. A loading rate of 600 pounds per minute was used. Each specimen was broken once on a four-inch span and, using the pieces from the first break, twice on a two-inch span.

The strengths of the fired bars are presented as firing contours in Figures 2, 3, and 4. The contour for two atmosphere steam firing is not complete but does extend to the point of maximum strengthening. For comparison, the 2100°F strength profiles for air, one atmosphere steam, and two atmosphere steam are shown in Figure 5.
Figure 2. Modulus of Rupture Contour for Slip Cast Fused Silica Fired Under One Atmosphere of Air.
Figure 3. Modulus of Rupture Contour for Slip Cast Fused Silica Fired Under One Atmosphere of Steam.
Figure 4. Modulus of Rupture Contour for Slip Cast Fused Silica Fired Under Two Atmospheres of Steam.

NOTE: Dashed line represents conditions for maximum strengthening.
Figure 5. Strengthening Curves for Slip Cast Fused Silica Fired at 2100°F in Air and in Steam.
c. Effects of Firing Conditions on Porosity and Bulk Density:

Prior to modulus of rupture testing, the porosity, bulk density, and apparent theoretical density of each bar were determined by air displacement. The porosity and bulk density profiles are shown in Figures 6 through 11. For comparison, the porosity and bulk density profiles for air and steam firing at 2100°F are shown in Figures 12 and 13.

The bulk properties of slip cast fused silica fired in steam and in air are noticeably different. While the porosity reaches a minimum and then begins to increase with increasing firing time in air, no such minimum has yet been found in steam firing. Since a maximum is observed in the strengthening profiles in steam firing and since the bulk densification rates above the point of maximum strengthening do not differ markedly in air and steam, this cannot be taken to indicate that steam accelerates viscous flow more than devitrification. A more likely explanation is that steam promotes the closing of pores by maintaining sintering at a higher rate than air. In spite of this, and the concomitant continuous porosity decrease, the flaws produced by thermal shock of the devitrified areas are still quite effective in reducing strength, resulting in a strength maximum even in the absence of a porosity minimum. This view is supported by the failure of the apparent theoretical density to increase in a manner consistent with devitrification in steam firing in contrast to the consistent increase in air firing.

Figure 6. Porosity of Slip Cast Fused Silica Fired Under One Atmosphere of Air.
Figure 7. Porosity of Fused Silica Fired Under One Atmosphere of Steam.
Figure 8. Porosity of Slip Cast Fused Silica Fired Under Two Atmospheres of Steam.
Figure 9. Bulk Density of Slip Cast Fused Silica Fired Under One Atmosphere of Air.
Figure 10. Bulk Density of Slip Cast Fused Silica Fired Under One Atmosphere of Steam.
Figure 11. Bulk Density of Slip Cast Fused Silica Fired Under Two Atmospheres of Steam.
Figure 12. Porosity Profiles for Slip Cast Fused Silica Fired at 2100°F in Air and Steam.
Figure 13. Bulk Density Profiles for Slip Cast Fused Silica Fired at 2100°F in Air and Steam.
The bulk density curves of Figure 13 are of particular interest. The initial sintering rate in one atmosphere air is seen to be higher than that in one atmosphere steam although the rate is maintained in steam but not in air. This difference is explained if the early sintering mechanisms are plastic flow and viscous flow, respectively, in air and steam.

A second point of interest is that there is an apparent shift in the sintering rate in steam at approximately the time of maximum strengthening. Since devitrification is a surface phenomenon, its first stage should involve growth of cristobalite patches on the surface of each particle until the entire surface layer is devitrified. Close correspondence of the time at which this occurs to the time of maximum strengthening would not be surprising. At this point, a shift would be likely in the sintering mechanism as the initial viscous flow at the particle surface is blocked by the continuous cristobalite layer. Following this blockage, the sintering mechanism could become any of the less rapid processes such as bulk diffusion, surface diffusion, vaporization and condensation, etc. This would produce the relatively abrupt change in the sintering rate noted in steam firing. Unfortunately, the data presently available do not permit identification of the second stage of steam sintering. A similar shift in sintering mechanism could occur in air firing but the normal continuous decrease in sintering rate with plastic flow would mask this effect.

Since air firing at one atmosphere produces more rapid initial sintering than one atmosphere steam firing, it would be interesting to examine the sintering rate in two atmosphere air. This rate might well be faster initially than the rate in two atmosphere steam. Firing in other atmospheres, such as ammonia or carbon dioxide, which might bridge with silica would also be of interest. Such additional firing techniques will be studied briefly if time and funds permit.

d. Activation Energy Analysis:

Methods were developed for estimation of the activation energies of a number of thermally activated transport processes in the firing of slip cast fused silica. These activation energies are summarized in Table II.

### TABLE II

**ACTIVATION ENERGIES FOR VARIOUS TRANSPORT PROCESSES IN THE SINTERING OF SLIP CAST FUSED SILICA**

<table>
<thead>
<tr>
<th>Process</th>
<th>Atmosphere</th>
<th>Pressure (Atm. Abs.)</th>
<th>Activation Energy (Kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintering</td>
<td>Air</td>
<td>1</td>
<td>69</td>
</tr>
<tr>
<td>Sintering</td>
<td>Steam</td>
<td>1</td>
<td>110</td>
</tr>
<tr>
<td>Sintering</td>
<td>Steam</td>
<td>2</td>
<td>120</td>
</tr>
<tr>
<td>Maximum Strength(^1)</td>
<td>Air</td>
<td>1</td>
<td>205</td>
</tr>
<tr>
<td>Sintering Rate Shift(^1)</td>
<td>Steam</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>Maximum Strength(^1)</td>
<td>Steam</td>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>Devitrification</td>
<td>Steam</td>
<td>1</td>
<td>98</td>
</tr>
</tbody>
</table>

1. Should be related to first formation of continuous cristobalite layer on particle surfaces. May be complex function of sintering rate, devitrification rate, and diffusion rate.
The activation energies in Table II must be supplemented in order to clarify the differences in steam and air firing. A few points are suggested, however. Steam apparently effects its improvement in overall sintering kinetics through a decrease in the viscosity of the silica rather than by decreasing the sintering energy barrier. This is indicated by the higher sintering activation energy in steam than in air. The effectiveness of steam in bringing this improvement about is indicated by the significant decrease in maximum strength activation energy accompanying steam firing.

Pressure apparently has little influence on the sintering process energetics as indicated by the similarity in the activation energies in one and two atmosphere steam. Again, the improved sintering in two atmosphere steam apparently results from a decrease in the resistance to flow rather than a decrease in the energy barrier.

The rough correspondence of the sintering, sintering rate shift, and devitrification activation energies for one atmosphere steam and the sintering and strengthening activation energies for two atmosphere steam tentatively indicates that sintering, strengthening, and devitrification are closely related transport processes. This is not surprising since all three processes are probably manifestations of the movement of silica tetrahedra.
e. Analysis of Early Devitrification Process:

Final x-ray diffraction analyses were begun to determine the bulk cristobalite growth rates during devitrification of slip cast fused silica. An analysis of the probable growth mechanism indicated that the initial growth stages should produce a cubic time variation in the cristobalite content. The preliminary cristobalite analyses for air and one atmosphere steam firing are shown as a function of firing time according to this criterion in Figures 14 and 15.

The preliminary data indicate that the initial devitrification does follow a cubic time variation up to approximately 10 per cent cristobalite. Extrapolation of both the steam and air data to zero firing time shows that the slip is not free of cristobalite. This initial cristobalite content appears, from both steam and air data, to be approximately 0.5 per cent.

3. Effects of Pressure and Vibration During Casting

A study was made of the changes in the properties of slip cast fused silica resulting from the application of pressure to the casting slip and vibration of the mold. Pressures of 0, 20, 40, and 60 psig were investigated in combination with 60 cps axial vibrations of 0, 0.010, 0.012, and 0.015-in. amplitude. The approximate casting times were measured, the porosities were determined by air displacement, and the dry moduli of rupture were measured in three point loading. Each bar was broken three times, once on a four inch span and twice on a two inch span using the pieces from the first break. Since the moduli of rupture in the unfired condition were low, a small deadweight lever machine was used for the strength measurements. The results of these studies are shown in Figures 16 through 18.
Figure 14. Cristobalite Content of Slip Cast Fused Silica Fired Under One Atmosphere of Air.
Figure 15. Cristobalite Content of Slip Cast Fused Silica Fired Under One Atmosphere of Steam.
Figure 16. Time Required to Cast a 3/4" Diameter Fused Silica Bar as a Function of Applied Pressure.
Figure 17. Porosity of Slip Cast Fused Silica as a Function of Casting Conditions.
Figure 18. Dry Modulus of Rupture of Slip Cast Fused Silica as a Function of Casting Conditions.
An increase in the casting pressure produced a significant decrease in casting time which was not altered by axial vibration. Vibration of the mold permitted more effective packing of the silica particles, resulting in decreased porosity, but this effect was more than offset by the increase in casting fluid velocity at even the lowest casting pressure increase. The dry strength of the cast bars varied in a manner consistent with the cast density and porosity. More efficient packing produced both lower porosity and higher dry strength as would be expected.

Since greater uniformity would presumably result from the improved speed of the pressure casting, the technique deserves further attention. Firing studies will be made to detect influences of pressure application on the sintering kinetics of cast bars. Since the majority of the increased speed is realized with the application of 20 psig, the firing studies will be restricted to the low pressure range.

B. Al-U$_3$O$_8$ Interactions

During the past year, a reorientation of this investigation has occurred. Emphasis has been shifted, at the sponsor's request, from a study of Al-U$_3$O$_8$ reactions as a fabrication technique to the development of data to aid evaluation of Al-U$_3$O$_8$ fuel dispersion stability. This change has necessitated the modification of certain experimental systems with a resultant impairment in the continuity of the investigation. The transition has now been completed and the modified study can be expected to proceed with increasing efficiency.
1. High $U_3O_8$ Composites

   a. Effects of Baymal Additions:

   A brief study made earlier indicated that additions of small amounts of Baymal$^1$ improved the uniformity of Al-$U_3O_8$ pellets prepared by powder metallurgy but did not affect the ignition characteristics. In order to evaluate this observation more concretely, three sets of 85.4 w/o $U_3O_8$ pellets were pressed, one set with no Baymal, one with 0.1 w/o Baymal, and one with 1 w/o Baymal. These pellets were subjected to DTA (differential thermal analysis) at a heating rate of 60°F per minute in 15 psig argon. The results of these tests are summarized in Table III.

   TABLE III

   EFFECT OF BAYMAL ADDITIVE ON IGNITION CHARACTERISTICS OF Al-85.4w/o $U_3O_8$ COMPOSITE

<table>
<thead>
<tr>
<th>Baymal Additive (w/o)</th>
<th>Reaction Temperature (°F)</th>
<th>Peak Height (mv)</th>
<th>Peak Area (mv-sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1650</td>
<td>2.20</td>
<td>102</td>
</tr>
<tr>
<td>0.1</td>
<td>1660</td>
<td>2.53</td>
<td>112</td>
</tr>
<tr>
<td>1.0</td>
<td>1640</td>
<td>2.05</td>
<td>79</td>
</tr>
</tbody>
</table>

   The results of the DTA tests were subjected to statistical analysis by t tests of the averages. These tests failed to show significance in the apparent differences between the 0 and 0.1 w/o Baymal pellets at greater than the 90 per cent level of confidence, possibly because of the

1. E. I. DuPont hydrated colloidal alumina.
small number of samples involved. The apparent decrease in all three reaction characteristics in the 1 w/o Baymal pellets did, however, show significance at greater than the 95 per cent level of confidence.

The results of the Baymal tests are far from conclusive. In order to produce concrete results, a greatly expanded study would be required since the pellets show considerable variability in reaction characteristics. Such a study may be warranted, however, by the implication that alumina may suppress Al-U₃O₈ reactions.

In spite of the doubt left by the Baymal study, the results appear sufficiently conclusive to justify halting Baymal addition as a mixing aid. Powder metallurgy pellets no longer are blended with Baymal.

b. Effects of U₃O₈ Particle Size:

In high U₃O₈ pellets studied previously, the particle size of the U₃O₈ showed a significant influence on the reaction characteristics indicated by DTA. Pellets containing more than 50 v/o U₃O₈ would be expected to show a decreased reaction tendency with coarse U₃O₈ since the mismatch in particle size with the fine (average 7μ) aluminum would lead to poor interphase contact. A decrease in U₃O₈ particle size should improve interphase contact in these pellets and lead to higher reaction tendencies. Such a result was observed in 85.4 w/o U₃O₈ pellets¹.

In pellets containing less than 40 v/o U₃O₈, the continuous aluminum matrix should be capable of coating the U₃O₈ particles completely. The interphase contact should thus be good across the entire U₃O₈ particle size spectrum and the reaction characteristics should reflect only the effects of increased reactive.

¹. Summary Report No. 1, p. 42.
surface area with decreasing particle size. As a result, the reaction characteristics should be less dependent on oxide particle size than in higher U₃O₈ pellets in which both surface area and contact effects would be significant.

A study of particle size effects was made in 75 w/o (49.8 v/o) U₃O₈ pellets. Spencer fused U₃O₈ was separated into six particle size fractions by screening in a Syntron sieve shaker and blended with Alcoa 140 atomized aluminum. The pellets were subjected to DTA at a heating rate of 60°F per minute in 15 psig argon. The results of the DTA tests are summarized in Table IV.

**TABLE IV**

**EFFECT OF U₃O₈ PARTICLE SIZE ON IGNITION CHARACTERISTICS OF Al-75 w/o U₃O₈ COMPACTS**

<table>
<thead>
<tr>
<th>Particle Size (mesh)</th>
<th>Reaction Temperature (°F)</th>
<th>Peak Height (mv/gm)</th>
<th>Peak Area (mv-sec/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+100</td>
<td>1810</td>
<td>0.234</td>
<td>9.05</td>
</tr>
<tr>
<td>-100 + 140</td>
<td>1810</td>
<td>0.206</td>
<td>5.09</td>
</tr>
<tr>
<td>-140 + 200</td>
<td>1810</td>
<td>0.223</td>
<td>7.55</td>
</tr>
<tr>
<td>-200 + 270</td>
<td>1840</td>
<td>0.209</td>
<td>6.33</td>
</tr>
<tr>
<td>-270 + 325</td>
<td>1830</td>
<td>0.235</td>
<td>6.69</td>
</tr>
<tr>
<td>-325</td>
<td>1790</td>
<td>0.242</td>
<td>10.52</td>
</tr>
</tbody>
</table>
Statistical analysis was applied to the results of the differential thermal analysis tests. This analysis did not show significant differences in ignition temperature and peak area in the particle size range above 325 mesh or in peak height across the entire particle size range. The -325 mesh samples did show significantly lower ignition temperatures and high peak areas. This would indicate more complete reactions in the -325 pellets probably as a result of the increase in reactive surface area. As expected, the effects of $U_3O_8$ particle size were far less significant in the 75 w/o $U_3O_8$ pellets than in the 85.4 w/o pellets previously tested.

2. Low $U_3O_8$ Composites

   a. DTA Tests:

Previous studies of composites containing less than about 60 w/o $U_3O_8$ failed to show definite reaction temperatures during DTA. This was thought to be due principally to the low sensitivity of the testing system which was designed for the more energetic low aluminum composites. As a part of the modified program, efforts were made to provide indications of reactions in dilute dispersions by DTA. This necessitated conversion of the DTA system to increase its sensitivity.

In the investigations of high $U_3O_8$ composites, platinum-13% rhodium 87% platinum thermocouples were used in view of the high temperatures reached during ignition. The thermocouples were contained within closed alumina spaghetti to avoid shorting from the aluminum vapor evolved upon ignition. Since these practices resulted in a drastically decreased sensitivity, the first step taken was to attempt to provide sufficient system sensitivity simply by using uncovered thermocouples with higher output coefficients.
No difficulties from high ignition temperatures or aluminum evaporation were anticipated in view of the much lower volumetric energy release expected in the dilute dispersions. The first thermocouple chosen for trial was chromel-alumel. The testing furnace was fitted with Conax packing glands to accept bare thermocouple wire and chromel-alumel couples were used for the standard and unknown posts. The platinum-rhodium control thermocouples were not changed.

In order to check the sensitivity of the modified system, a series of 75 w/o $U_3O_8$ pellets was pressed using "dead-burned" Y-12 $U_3O_8$ supplied by the Metals and Ceramics Division, Oak Ridge National Laboratory. The pellets were tested in 15 psig argon at a heating rate of 60°F per minute. Ignition occurred at an average temperature of 1780°F, the same value indicated by platinum-rhodium thermocouples. The system sensitivity seemed to be roughly an order of magnitude greater than before modification.

Several 50 w/o $U_3O_8$ pellets were pressed using Y-12 oxide. These pellets were tested in the modified system at a heating rate of 60°F per minute using a pressed alumina standard as in the DTA tests of high $U_3O_8$ specimens. The DTA curve fluctuated wildly during heating but an apparent ignition at approximately 1800°F were noted.

The wide fluctuations in the DTA curve might have been expected from the nature of the composite. The aluminum content was high enough (75.2 w/o) to provide a somewhat higher thermal conductivity than in most of the pellets studied before. This higher thermal conductivity altered the heating rate in the unknown to the point that alumina was no longer a satisfactory standard. For most purposes, except for calorimetry, the ideal standard would have the same thermal diffusivity as the unknown and would also contain the same amount
of aluminum as the unknown. This would provide equal thermal arrests during aluminum melting in both standard and unknown, cancelling out the melting endotherm, and permitting observation of any lower temperature exotherms which might exist.

Although obtaining standards with suitable thermal diffusivity and aluminum content would be a rather lengthy program in itself, brief studies were made to select a better standard than pressed alumina. Several standard pellets were studied including inert low conductivity metals, Al-Al$_2$O$_3$ mixtures with the same volume content of aluminum as the unknown, previously fired Al-U$_3$O$_8$ dispersions, and graphite. Although none of these materials was completely satisfactory, the pre-fired Al-U$_3$O$_8$ and graphite standards produced useful curves. Representative curves obtained using specimens cut from a rolled plate of ATR composition 1 are shown in Figure 19.

The DTA curves obtained with graphite and pre-fired Al-U$_3$O$_8$ standards are similar in most respects. In testing ATR specimens, an exotherm occurs on heating, peaking at 1320 - 1360°F. This exotherm, large with a prefired Al-U$_3$O$_8$ standard and small with a graphite standard, may be due to a low temperature reaction. Such a reaction would be masked by the aluminum melting endotherm, more with the graphite standard than with the Al-U$_3$O$_8$ standard in which the excess aluminum remaining in the reacted standard would partially cancel the aluminum endotherm in the unknown. This apparent low temperature exotherm, instead of representing a reaction, could result simply from changes in the thermal diffusivity accompanying melting of the aluminum.

1. 33.79 w/o U$_3$O$_8$, 66.07 w/o X-800 aluminum, 0.14 w/o B$_4$C. Hot rolled at 500°C to 8:1 reduction ratio followed by 15 per cent cross roll. Vacuum annealed 1 hour at 500°C.
Figure 19. DTA Curves of ATR Specimens Run Against Graphite and Fired ATR Standards.
The low temperature exotherm is followed by a large endotherm, peaking at 1400-1500°F, taken as the aluminum melting endotherm. This endotherm, according to rough calculations, could peak approximately 250°F after the standard passes the aluminum melting point. This large differential would result from the greater free aluminum content in the unknown than in the standard.

On heating past the aluminum melting endotherm, a second exotherm occurs, usually peaking at 1800-1900°F. During this exotherm, the unknown may be seen to glow more brightly than the standard.

Although the standards other than pre-fired Al-\(\text{U}_3\text{O}_8\) dispersions and graphite failed to yield satisfactory DTA curves, all showed the aluminum melting endotherm and the high temperature reaction exotherm.

Attempts were begun to extend the DTA test to at least semi-quantitative analysis of the extent of reaction in heated \(\text{Al-}\text{U}_3\text{O}_8\) compacts. A series of samples was prepared from the rolled ATR fuel plate. These specimens were subjected to DTA under argon at a heating and a cooling rate of 60°F per minute. A previously fired ATR specimen was used as the standard. Following DTA, measurements were made of the DTA chart peak areas corresponding to the aluminum melting endotherm and the 1800°F reaction and aluminum solidification exotherms. The complete x-ray diffraction trace was determined for each specimen. Reduced data from this study are summarized in Table V.
### REDUCED DATA FOR ATR SPECIMENS

<table>
<thead>
<tr>
<th>Sample&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Reaction Exotherm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Al Cooling Exotherm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Al Heating Endotherm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>U&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt; Area Ratio&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Total&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41-16</td>
<td>---</td>
<td>0.744</td>
<td></td>
<td>2.44</td>
<td>1.80</td>
</tr>
<tr>
<td>40-16</td>
<td>---</td>
<td>0.824</td>
<td></td>
<td>2.05</td>
<td>1.67</td>
</tr>
<tr>
<td>42-16</td>
<td>---</td>
<td>0.733</td>
<td></td>
<td>2.13</td>
<td>2.03</td>
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<tr>
<td>39-16</td>
<td>---</td>
<td>0.532</td>
<td></td>
<td>1.81</td>
<td>1.69</td>
</tr>
<tr>
<td>44-F</td>
<td>0.173</td>
<td>0.0</td>
<td></td>
<td>1.07</td>
<td>0.53</td>
</tr>
<tr>
<td>48-F</td>
<td>0.211</td>
<td>0.236</td>
<td></td>
<td>1.27</td>
<td>0.77</td>
</tr>
<tr>
<td>46-F</td>
<td>0.234</td>
<td>0.071</td>
<td></td>
<td>1.16</td>
<td>0.61</td>
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<tr>
<td>45-F</td>
<td>0.249</td>
<td>0.169</td>
<td></td>
<td>1.26</td>
<td>1.03</td>
</tr>
<tr>
<td>47-F</td>
<td>0.250</td>
<td>0.075</td>
<td></td>
<td>1.11</td>
<td>0.80</td>
</tr>
</tbody>
</table>

<sup>1</sup> -16 = Terminal DTA temperature of 1600°F. Arranged in order of decreasing U<sub>3</sub>O<sub>8</sub>.

<sup>2</sup> -F = Terminal DTA temperature above reaction exotherm (~1900°F). Arranged in order of increasing reaction exotherm peak area.

<sup>2</sup> Relative x-ray peak area compared with 21.5° peak.
The arrangement of Table V should correspond roughly to increasing conversion of $U_3O_8$. A general, but by no means totally consistent or quantitative trend toward lower aluminum exotherm:endotherm ratios is observed. This trend appears promising enough to warrant an expanded study to permit statistical analysis. At any rate, significant difference in the exo-endotherm ratio obviously exists between the -16 and -F group as would be expected. The x-ray data show a trend toward higher $UO_2$ contents in the more strongly reacted samples as well as a reasonable qualitative correspondence between high $UO_2$ and high $UA_2$. A possible explanation for the lack of correlation of $U_3O_8$ with the reaction products and the reaction exotherm peak areas is apparent in the $U_3O_8$ diffraction peak area ratios. The absence of constant area ratios indicates either significant matrix absorption differences, varying $U_3O_8$ preferred orientation, or more likely, shifts in the oxide stoichiometry.

In view of the difficulties experienced with x-ray analysis for $U_3O_8$, the advantages of successful reaction extent survey by DTA are even more apparent. While such an analytical technique would be useful only for total reaction surveys, not for dynamic rate studies, the time savings and independence of oxide structure effects would make the DTA approach, where applicable, compare most favorably with post-heating diffraction analysis.

Investigations were begun to determine the feasibility of DTA calorimetry of the Al-$U_3O_8$ reaction. Such an approach could provide only rough accuracy but the expense would be minimal compared with more conventional calorimetry. The technique being investigated involves only routine DTA runs. An inert standard is used to display the entire aluminum melting endotherm. The peak area of the endotherm is used as an internal standard, with the known
heat of fusion of aluminum, to calibrate each DTA chart individually. Based on this calibration, the reaction exotherm energy is given simply by

\[ E = x\Delta h_f \frac{A_R}{A_M} \]

where

- \( E \) = Reaction energy release per gram of sample.
- \( x \) = Weight fraction of aluminum in original sample.
- \( \Delta h_f \) = Heat of fusion of aluminum.
- \( A_R \) = DTA reaction peak area.
- \( A_M \) = DTA aluminum melting endotherm peak area.

If this technique can be reduced to practice, the usual problems associated with DTA calorimetry will be minimized. A complex, expensive DTA furnace will not be required, the DTA samples and standard pellets will not have to be the same size or precisely matched, sample and standard orientation need not be precisely reproducible, and no separate system calibration need be made.

For DTA calorimetry by this technique, the pre-fired Al-U$_3$O$_8$ standard is not suitable since the entire aluminum melting endotherm must be displayed. As a result, graphite standards were used in the initial tests. The cylindrical standard pellets were machined from spectrographic graphite rods. The standards were vacuum annealed for several hours at 2100°F to remove any volatile contaminants and stored in a dessicator. DTA tests were begun using these standards with parallelepiped samples cut from ATR fuel plate.

Although only two tests have been made to date, the results are sufficiently interesting to be reported. The data from the two graphite standard runs made to date are summarized in Table VI.
### TABLE VI
**INITIAL DTA CALORIMETRY RESULTS**

<table>
<thead>
<tr>
<th></th>
<th>Sample G-1</th>
<th>Sample G-2</th>
</tr>
</thead>
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<tr>
<td>Sample Weight (gm)</td>
<td>3.86</td>
<td>3.81</td>
</tr>
<tr>
<td>Reaction Peak Temperature (°F)</td>
<td>1840</td>
<td>1850</td>
</tr>
<tr>
<td>Aluminum Melting Endotherm</td>
<td></td>
<td></td>
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<tr>
<td>Peak Area (in²)</td>
<td>2.96</td>
<td>2.70</td>
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<tr>
<td>Aluminum Solidification</td>
<td></td>
<td></td>
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<tr>
<td>Exotherm Peak Area (in²)</td>
<td>1.93</td>
<td>1.76</td>
</tr>
<tr>
<td>Apparent Aluminum Conversion (%)</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Reaction Exotherm Peak Area (in²)</td>
<td>1.01</td>
<td>0.75</td>
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<tr>
<td>Apparent Reaction Energy Release (Mw-sec/kg)</td>
<td>0.059</td>
<td>0.072</td>
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<tr>
<td>Theoretical Maximum Energy Release (Mw-sec/kg)</td>
<td></td>
<td>0.62</td>
</tr>
<tr>
<td>Theoretical Maximum Aluminum Conversion (%)</td>
<td></td>
<td>28.4</td>
</tr>
</tbody>
</table>

1. Assuming \( \% \text{ conversion} = (1 - \frac{\text{Exotherm Area}}{\text{Endotherm Area}}) \times 100 \)
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The principal difficulty encountered in making the calculations for Table VI lay in proper selection of the DTA base line. As a result of the high thermal diffusivity of the material and the impossibility of matching the sample and standard diffusivities exactly, no regular base line appeared on the chart. Although a better choice can be made with further study, the line chosen for the first runs was a heating base line parallel to the cooling line. Since this involves several assumptions, including those of no reaction during cooling and a constant sample thermal diffusivity prior to and following the upper reaction zone, this is almost certainly not the proper choice. The values calculated from this assumed base line do, however, seem gratifyingly reasonable when compared with the theoretical limits. Consideration of the probable direction of error in the base line choice would indicate that the true base line is probably more nearly vertical than the one arbitrarily selected. This would tend to increase the calculated value for the integrated energy release and decrease the value of the aluminum conversion, bringing both more in line with the theoretical values. It is of possible interest to note that selection of a vertical base line would bring the aluminum conversion values to approximately 17.5 per cent, a quite reasonable figure.
b. Metallography:

Metallographic examination of the ATR specimens was begun. Of the preparation techniques investigated to date, relief polishing has provided the most clear results. Phase identification has not progressed far enough to warrant reproduction of a series of micrographs but typical examples are shown in Figure 20. Increasing reaction appears as an increase in concentration of the white phase obvious in both micrographs. This phase is seen, from the partially reacted specimen, to grow around the U₀.₃₀ particles.

Speculative identification of the reaction products in the micrographs is very difficult. Its location and distribution imply that it is an intermetallic compound but this is far from certain. Similar samples are now being studied by electron microprobe analysis and microhardness determination and identification should be possible in the near future.

c. Strength of Molten ATR Composites:

Attempts were made to provide rough indications of the load-bearing capability of ATR composites at elevated temperatures. A vertical 1/4-in. outside diameter tube was passed through the floor of a DTA furnace. An ATR specimen, 1/2-in. square by approximately 90 mils thick, was placed over the open end of the tube. The tube was valved through a manometer to the inside of the furnace and provisions were made to draw a controlled vacuum on the tube. Since, as melting occurred, the ATR specimen sealed the tube, a controlled pressure differential could be established between the slightly evacuated tube and the body of the furnace at 16 psi of argon. Following temperature equilibration, the pressure differential was produced and increased slowly until the sample could be seen to sag.
Figure 20. Microstructure of Fired ATR Composites.
In some cases, the specimen went on to rupture as soon as sag occurred. In others, the sag plugged the tube and no further deformation was obtained. The results of this sag test are summarized in Table VII.

**TABLE VII**

PRESSURE DIFFERENTIAL REQUIRED TO PRODUCE SAG IN ATR COMPOSITES

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Testing Temperature (°F)</th>
<th>Specimen Thickness (mils)</th>
<th>Pressure Differential Required to Produce Sag (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>1350</td>
<td>93</td>
<td>1.1</td>
</tr>
<tr>
<td>15</td>
<td>1380</td>
<td>93</td>
<td>0.6</td>
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<td>16</td>
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<td>90</td>
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<tr>
<td>17</td>
<td>1350</td>
<td>85</td>
<td>0.6</td>
</tr>
<tr>
<td>18</td>
<td>1700</td>
<td>95</td>
<td>0.7</td>
</tr>
<tr>
<td>19</td>
<td>1710</td>
<td>90</td>
<td>0.9</td>
</tr>
<tr>
<td>20</td>
<td>1710</td>
<td>90</td>
<td>0.9</td>
</tr>
<tr>
<td>21</td>
<td>1860&lt;sup&gt;1&lt;/sup&gt;</td>
<td>90</td>
<td>&gt; 4&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>22</td>
<td>1860&lt;sup&gt;1&lt;/sup&gt;</td>
<td>85</td>
<td>&gt; 4&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

1. Specimens permitted to fire prior to application of pressure differential.
While it is obvious that the data of Table VII are not conclusive or accurate, they appear uniform enough to confirm that the unreacted Al-\(\text{U}_3\text{O}_8\) composites do possess some strength even molten. The strength does not decrease much, if at all, in the temperature range between melting and rapid reaction. In addition, the reacted specimens are substantially stronger at temperature than unreacted specimens.

Preliminary metallography of the sag specimens indicated rather peculiar behavior. A typical specimen is illustrated in Figure 21. The macrograph shows that the displaced mass of material is apparently almost free of oxide. This observation is confirmed by the micrographs which show that the exuding material left the oxide behind.

The implications of the macro- and micrographs are most interesting. The apparent exfiltration of the oxide free aluminum may indicate that the \(\text{U}_3\text{O}_8\) is linked in a continuous network, possibly of \(\text{Al}_2\text{O}_3\), and/or stringered \(\text{U}_3\text{O}_8\). Failure of the specimen under a pressure differential could proceed by collapse of this network after exfiltration of a significant amount of aluminum. The presence of such an oxide network could account for the failure of the specimens to weaken significantly with increasing temperature. In addition, reinforcement of the oxide network upon Al-\(\text{U}_3\text{O}_8\) reaction could account for the substantial increase in strength at temperature following reaction.

If an oxide network does exist in the ATR specimens, some consideration must be given to the effects of loading rate on the strength at temperature. Rapid load application might produce a higher temporary strength since the aluminum would not have time to "exfiltrate" and weaken the structure. If the load-bearing capacity of the ATR dispersion is of design importance, a need for more detailed studies may be indicated.
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d. X-ray Study of Al-$\text{U}_3\text{O}_8$ Reaction Kinetics:

A furnace was constructed to adapt the high temperature x-ray diffraction system to dynamic Al-$\text{U}_3\text{O}_8$ reaction rate measurements.

The high temperature diffraction equipment consists of a Siemens Crystalloflex IV x-ray generator, North American Philips Co. diffractometer, proportional counter, and Siemens counting equipment including a strip chart recorder. The x-ray tube is a Philips high intensity copper tube, and $K_\alpha$ radiation is used.

The high temperature furnace is illustrated in Figures 22 and 23. It is a more refined version of a furnace used in earlier work on this project. The furnace body is cut from foamed fused silica, and the heated cavity is a cube measuring approximately two inches on a side. The heaters are 0.040-in. diameter Kanthal A-1 resistance wire, coiled and placed around lengths of 3/16-in. diameter alumina spaghetti. The upper and lower halves of the furnace were fabricated separately, and the heaters in each half connected in series. About 200 inches of heating wire were put into the furnace. Power is furnished through vacuum glands in the aluminum end plate and brought by copper wire to the right end of the furnace body (see Figure 22), where the copper leads are connected to the Kanthal heating wire.

Two platinum, platinum - 13% rhodium thermocouples, prepared from 0.020-in. diameter wire and supported by alumina spaghetti, extend through the roof of the heated cavity and are positioned very close to the specimen. These are connected to temperature compensated lead wires which extend through vacuum glands in the aluminum end plate. One thermocouple actuates a Wheelco Model 403 temperature controller (see Figure 24), and the other permits the temperature to be monitored.

Figure 22. High Temperature X-ray Diffraction Furnace.
Figure 23. Rear View of High Temperature X-ray Diffraction Furnace Showing Vacuum Vessel.
Figure 24. High Temperature X-ray Furnace Control System.
by a potentiometer. The temperature can also be measured with an optical pyrometer focused on the sample through one of the Mylar x-ray windows.

The sample rests on a slip cast and fired alumina platform supported by two 3/16-in. diameter alumina rods.

The furnace is designed for operation with a controlled atmosphere. The stainless steel vacuum vessel shown in Figure 22 is placed over the furnace body and sealed at the aluminum back plate with a neoprene gasket. The system is evacuated with a mechanical pump and then filled with helium or argon to an absolute pressure slightly above 1 atmosphere. The vacuum vessel is equipped with 0.001-in. thick Mylar x-ray windows. These are held in place by aluminum clamps and sealed with neoprene gaskets.

Cooling water is circulated through copper tubing attached where high temperatures are likely to be a hazard to the equipment.

The furnace is designed for use at diffraction angles (2θ) of 0 to 60°, which is adequate for thermite analyses. Provisions are made for adjustment of the sample elevation and orientation.

In preliminary runs with Al-U₃O₈ specimens, the high temperature diffraction system performed quite well. Following the preliminary runs, however, two sources of trouble arose which have caused a significant delay to this phase of the program.

Difficulties were first encountered when the counting tube became inoperative. In the interval since the diffraction system was purchased, Siemens altered the design of the counting tube and the new tube did not fit the old holder. Replacement of the tube and machining of an adapter resulted in a delay of three weeks.
Following restoration of the diffraction system to operation, runs were resumed only to be halted again by an unexpected bloating of the specimen during heating, resulting in blockage of the diffraction beam. This difficulty has not yet been resolved. Factors being examined are leakage into the furnace, failure of the silica insulation to outgas, internal contamination from sulfur, halogens, etc., and contamination of the helium filler gas. Every effort is being made to determine the source of bloating so that the study can be resumed as soon as possible.

3. Comparison of Al-UO$_2$ and Al-U$_3$O$_8$ Compacts

Studies were begun to compare reaction tendencies in Al-UO$_2$ and Al-U$_3$O$_8$ powder metallurgy compacts. Compacts containing 35 w/o UO$_2$ and 35 w/o U$_3$O$_8$ were produced by powder metallurgy. The starting materials were Alcoa 140 atomized aluminum, hydrothermal UO$_2$, and "dead-burned" U$_3$O$_8$. The pellets were subjected to differential thermal analysis in argon at a heating rate of 60° F per minute.

One of the Al-UO$_2$ pellets failed to show a reaction peak although no malfunction in the equipment was detected. This datum point was omitted from the summary of the DTA results given in Table VIII.

From the preliminary results, it appears that Al-U$_3$O$_8$ compacts undergo reaction at a lower temperature than Al-UO$_2$ compacts under the conditions of the DTA test. The reaction appears more energetic in the Al-UO$_2$ compacts, however. While this could be explained in terms of a higher activation energy

---

1. Uranium oxides furnished through the courtesy of the Metals and Ceramics Division, Oak Ridge National Laboratory.
in Al-UO\(_2\) resulting in onset of the reaction at a higher temperature, and
greater reaction rates at this higher temperature following reaction onset,
these data are based on too few samples to be conclusive. Additional samples
will be run to permit statistical evaluation.

TABLE VIII

DTA DATA FOR AL-UO\(_2\) AND AL-U\(_3\)O\(_8\) COMPACTS

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature of Exotherm Peak (°F)</th>
<th>Peak Height (mv/gm)</th>
<th>Peak Area (in(^2)/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-35 w/o UO(_2)</td>
<td>1820</td>
<td>0.51</td>
<td>0.20</td>
</tr>
<tr>
<td>Al-35 w/o U(_3)O(_8)</td>
<td>1780</td>
<td>0.38</td>
<td>0.16</td>
</tr>
</tbody>
</table>
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IV. PERSONNEL

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Senior Investigator

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FINAL REPORT

PROJECT NO. B-153, TASK II

REACTIONS IN Al-34 w/o U3O8 DISPERSIONS

By J. D. Fleming, J. W. Johnson,

and S. H. Bomar

Prepared for
U. S. Atomic Energy Commission
Oak Ridge Operations Office
Oak Ridge, Tennessee

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1 July

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia
ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

FINAL REPORT
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J. D. Fleming, J. W. Johnson,
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U. S. Atomic Energy Commission
Oak Ridge Operations Office
Oak Ridge, Tennessee

1 July 1964
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FOREWORD

The investigation reported in this document was performed by the Engineering Experiment Station of the Georgia Institute of Technology under U. S. Atomic Energy Commission Contract No. AT-/(40-1)-2483. The work was sponsored by the Division of Reactor Development, Fuels and Materials Development Branch, Mr. J. M. Simmons, Chief. The contract was administered by the Oak Ridge Operations Office, Reactor Division, Dr. David F. Cope, Director.
I. INTRODUCTION

This program is the outgrowth of an earlier investigation of the fabrication of refractory fuel materials by exothermic sintering. With the discovery of rapid exothermic reactions in Al-U\(_3\)O\(_8\) dispersions of high U\(_3\)O\(_8\) content, interest was generated in the possibility of such reactions in lower U\(_3\)O\(_8\) dispersions such as those proposed as fuels for ATR and HFIR. This study was instituted to explore the reactions occurring in dispersions of approximately 34 w/o U\(_3\)O\(_8\) in aluminum. Primary attention was devoted to the kinetics of these reactions.
II. SUMMARY

Attempts were made to determine the reaction kinetics in dispersions of approximately 34 w/o $U_3O_8$ in aluminum heated above the melting point of aluminum. Techniques employed included differential thermal analysis, dynamic high temperature x-ray diffraction, and post-heating chemical analysis.

Reduction of the $U_3O_8$ was found to proceed in two stages, an early rapid reduction to $UO_2$ and a later slow reduction of the $UO_2$ to U-Al solution. None of the experimental techniques proved fast enough to reveal the kinetics of the rapid reduction to $UO_2$. During this rapid reaction, approximately 15 per cent of the $U_3O_8$ was reduced to U-Al solution and approximately 65 per cent of the $U_3O_8$ was reduced to $UO_2$ when the dispersion was heated, over a time of approximately two minutes, from 1300° F to 2000° F. Most of the reaction appeared to occur between 1700° and 1800° F. Following this initial reaction, further $U_3O_8$ reduction occurred at a rate estimated to be approximately 2 to 8 per cent per minute. During the early rapid reaction, the calculated energy release was approximately 100 to 200 kcal. per kg. of $U_3O_8$. During the subsequent slower reaction, the energy release rate was estimated to be 10 to 40 kcal. per minute per kg. of $U_3O_8$.

A brief study was made of the deformation under load of a dispersion of approximately 34 w/o $U_3O_8$ in aluminum at temperatures above the melting point of aluminum. Below 1800° F, approximately 1 psi static transverse pressure differential was required to produce gross deformation in the molten dispersion when the specimen thickness was approximately 90 mils. The deformation proceeded by exudation of oxide-free alloy from the dispersion. The load required to produce deformation did not vary significantly from 1350° to
1710° F. At 1860° F, the specimen reacted essentially completely before pressure application and deformation did not occur under a pressure differential of 4 psi, the maximum obtainable in the test apparatus.
III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Reaction Kinetics

Studies were made using a variety of techniques to evaluate the kinetics of Al-U₃O₈ reactions in dispersions containing approximately 3½ w/o U₃O₈. While none of these techniques proved capable of clearly displaying the reaction rates, taken as a whole the composite of the data does provide some guideline values.

1. DTA Studies

The first approach to the problem was differential thermal analysis. The principal difficulty encountered was selection of a suitable standard material. With increasing thermal diffusivity, the choice of a standard becomes much more critical if base-line drift and sporatic peaking is to be avoided. This problem was compounded in testing Al-U₃O₈ dispersions since, in addition to the behavior typical of a high thermal diffusivity material, a marked change in thermal diffusivity was noted as the reaction proceeded. In general, this caused a standard of sufficiently high diffusivity to match the unreacted dispersion to be of too high diffusivity to match the dispersion following reaction. While no really suitable standard was ever developed, the results from all of the moderately suitable standard materials were at least consistent. This is illustrated by the DTA traces shown in Figure 1 which were obtained with graphite and pre-fired Al-U₃O₈ dispersion standard pellets.

On both charts, an exotherm appears at an indicated standard midline temperature of 1320°-1360° F. This was conclusively demonstrated not to be a low temperature reaction by metallography and x-ray diffraction analysis.
Figure 1. DTA Curves of Al-U₃O₈ Specimens Run Against Graphite and Fired Al-U₃O₈ Standards.
of samples heated to this temperature range and cooled. This exotherm probably can be attributed to earlier melting of the aluminum in the Al-U₃O₈ standard pellet as well as changes in the thermal diffusivity.

Following the apparent exotherm, an endotherm occurred, peaking at approximately 1520° F standard midline temperature. A rough heat balance, equating the sensible heat into the standard with the latent heat to melt the aluminum in the unreacted dispersion, indicated that the specimen could lag the standard by 250° F during fusion of the aluminum. This brings the peak of the endotherm into good agreement with the melting point of aluminum. This observation is strengthened by the closely constant slope of the curve over the temperature range from 1300° to 1500° F.

In all cases, a higher temperature exotherm was observed, peaking at approximately 1850° to 1900° F. This was taken to be representative of the region of rapid reaction in the specimen.

Since the thermocouples were located in the center of the specimen and standard pellets, use of the DTA curves to yield reaction rates would be very speculative. An interesting trend can be observed, however, by treating the DTA tests as calorimetric determinations of the total energy release. This technique necessitated the use of an inert graphite standard, to display the entire aluminum melting endotherm. Since the DTA base line is very difficult to locate with a graphite standard, as a result of poorly matched thermal diffusivities, an inherent source of error is apparent. Aside from this, the remaining assumptions do not seem unreasonable. These assumptions center around taking the aluminum melting endotherm as an
internal calibration standard. If the heat transfer characteristics are assumed to be relatively constant during the portion of the cycle above the aluminum melting point, the measured endotherm area serves to calibrate the chart since the mass of aluminum in the specimen and the heat of fusion of aluminum are known. Based on this calibration, the reaction exotherm energy is given by

\[ E = x \Delta h_f \frac{A_R}{A_M} \]  

where

- \( E \) = Reaction energy release per gram of sample
- \( x \) = Weight fraction of aluminum in original sample.
- \( \Delta h_f \) = Heat of fusion of aluminum.
- \( A_R \) = DTA reaction peak area.
- \( A_M \) = DTA aluminum melting endotherm peak area.

The conversion of aluminum could also be calculated by,

\[ C = 1 - \frac{A_M}{A_S} \]  

where

- \( C \) = Fraction of aluminum reacted
- \( A_S \) = DTA aluminum solidification exotherm area.

Equation 2, however, assumes constant thermal diffusivity in the reacted and unreacted specimen. A comparison of the heating and cooling DTA curves
in Figure 1 shows that this is definitely untrue and use of Equation 2 is to be avoided.

In practice, the reaction exotherm area obtained using a graphite standard did not vary significantly from that obtained with a pre-fired ATR standard. As a result, and since only seven runs were made, the data for pellets run against graphite and against pre-fired ATR standards are grouped in Table I.

TABLE I

DTA "CALORIMETRY" RUNS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction Exotherm (in²/gm)</th>
<th>Aluminum Melting Endotherm (in²/gm)</th>
<th>Apparent Energy Release (kcal/kg U₃O₈)</th>
</tr>
</thead>
<tbody>
<tr>
<td>44-F</td>
<td>0.173</td>
<td>----</td>
<td>22</td>
</tr>
<tr>
<td>G-2</td>
<td>0.197</td>
<td>0.709</td>
<td>25</td>
</tr>
<tr>
<td>48-F</td>
<td>0.211</td>
<td>----</td>
<td>26</td>
</tr>
<tr>
<td>46-F</td>
<td>0.234</td>
<td>----</td>
<td>29</td>
</tr>
<tr>
<td>45-F</td>
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<td>30</td>
</tr>
<tr>
<td>47-F</td>
<td>0.250</td>
<td>----</td>
<td>31</td>
</tr>
<tr>
<td>G-1</td>
<td>0.262</td>
<td>0.767</td>
<td>31</td>
</tr>
</tbody>
</table>

Average Apparent Energy Release = 28 kcal/kg U₃O₈
In calculating the energy release for the specimens run against pre-fired ATR specimens, the average aluminum melting endotherm area for the two runs against graphite was used. This technique certainly cannot be claimed to be highly accurate but a much larger sample set would be required for statistical evaluation, at any rate, and the indicated trend is interesting for comparison with the results from other studies to be discussed later.

2. X-ray Diffraction Studies

The second technique applied to the investigation of Al-U$_3$O$_8$ reactions was high temperature x-ray diffraction. A furnace $^1$ was constructed to permit diffraction to be carried out during specimen reaction, providing a complete reaction history for a single sample. This technique was chosen to minimize, insofar as possible, sample to sample variations by following the entire reduction history $^2$ of each specimen, and permit statistical evaluation of the reaction kinetics with a much smaller set.

The first runs on the elevated temperature x-ray system were made using a rolled dispersion of 34 w/o U$_3$O$_8$. Specimens of this dispersion were run without difficulty for short times at low temperatures but attempts to increase either time or temperature produced profound macroscopic blistering and swelling in the sample. This gross deformation caused a loss of x-ray beam alignment and failure to obtain useful results.

The new dispersion was not obviously different from those used in earlier

---


$^2$"Reduction history," used for convenience throughout this report, means the amount of reduction as a function of time.
work in microstructure or composition except that spectrographic analysis showed no nickel. A detailed review of handling techniques failed to indicate any sources of difference in the production of this dispersion except that the compact may not have been outgassed prior to being rolled.

Attempts were made to eliminate the swelling by vacuum annealing. Annealing at 1200° F for one hour produced marked blistering. Annealing at 1100° F for one hour and at 1150° F for one hour decreased the incidence of blistering from 100 per cent to 20 per cent. No technique was developed which could eliminate the blistering completely.

Since earlier dispersions did not swell unduly, the occurrence of such pronounced swelling in the new material produced doubts as to its nature. In order to avoid possible erroneous results arising from undetected contaminants in the dispersion, the decision was made to discontinue using the new dispersion and substitute a reference ATR plate from the ORNL fabrication development study. Through the courtesy of ORNL, a plate was flattened and transmitted to Georgia Tech for x-ray studies.

Specimens were sheared from the plate and the cladding was removed from one side to expose the Al-U$_{0.8}$ fuel meat. High temperature x-ray runs were begun to determine the Al-U$_{0.8}$ reaction rate but difficulty was encountered in the first run as a result of the fluidity of the cladding on the unmachined side of the specimen at testing temperatures. The cladding on which the sample rested was sufficiently fluid to flow when the diffraction table was tilted to the required angle. This caused the fuel meat, which did not flow significantly, to change its orientation, with a resulting loss of beam alignment.
Several schemes were tried to make the fuel surface stable during the x-ray test. Removal of the cladding from both sides of the sample was impossible due to the thinness of the 20 mil fuel region. Mechanical restraint of the specimen was unsuccessful. The difficulty was finally solved by inverting the furnace, supporting the sample on the fuel meat surface on a loose mesh stainless steel grid held by alumina bars, and carrying out the diffraction below the horizontal axis of the goniometer. The fuel meat proved strong enough at the testing temperatures not to flow and beam alignment was retained.

The criterion established 1/ for evaluation of the x-ray system was that no more than three per cent of the $U_3O_8$ should react prior to the time the reaction rate could be monitored. The first few successful runs proved that the scanning speed of the diffraction system was inadequate to meet this criterion. Before the temperature equilibrated and the first scan could be made, the reaction was greater than three per cent complete at all temperatures above approximately 1600° F. Accordingly, the x-ray technique was abandoned after only a few runs.

Although the x-ray technique was discarded as a result of its insufficient speed, the results of the few tests made can be manipulated to indicate further trends. Diffraction and metallographic analyses indicate that the Al-$U_3O_8$ reaction proceeds in two stages. The first involves reduction according to the equation

$$\frac{4}{3} Al + U_3O_8 \rightarrow UO_2 + \frac{2}{3} Al_2O_3$$  \hspace{1cm} (3)

1/Established by Babcock and Wilcox from a consideration of the behavior of ATR during a power surge.
This reduction occurs at a rapid initial rate which quickly subsides, probably as a result of mechanical hinderance by the layer of UO₂ and Al₂O₃ which forms. Further reduction of the UO₂ occurs at a lower rate according to the unbalanced equation

\[ \text{UO}_2 + \text{Al} \rightarrow \text{U-Al}_{\text{(soln.)}} + \text{Al}_2\text{O}_3 \]  

(4)

A brief examination of the U-Al phase diagram shows that the reduced uranium was dissolved in the aluminum at testing temperature. Assuming high diffusivity of uranium in molten aluminum, U₁₃ could not form until the U₃O₈ was essentially completely reduced. This point is discussed further in a later section.

The x-ray diffraction trace obtained during reaction shows two stages. In the first, the UO₂ peak increases as more is formed by reduction according to Equation 3. At the same time, the U₃O₈ peak will diminish as U₃O₈ is reduced and, more important, as the forming UO₂ layer extinguishes the x-ray beam by mass absorption. In the second stage, the UO₂ peak diminishes through volume disappearance of UO₂ accompanying further reduction according to Equation 4. The diffraction pattern thus indicates a complete disappearance of U₃O₈ before it actually reacts completely. The point at which this occurs can be estimated by a mass absorption calculation. Using the mass absorption coefficients for U, O, and Al and the calculated stoichiometric composition of the barrier layer, the tenth value thickness is found to be 8.28 microns. For the average penetration angle for UO₂ diffraction, this produces a barrier thickness, equivalent to the tenth value layer, of 0.967 microns. This corresponds to 99% extinction of the Cu Kα.
radiation at a barrier thickness of 1.94 microns. If the particle size
distribution of the $U_3O_8$ were known, in the rolled dispersion, this could
be converted to an average conversion, according to Equation 3, by the
relationship,

$$ C_{avg} = \frac{\int_0^N 1 - \left( \frac{r - 1.94}{r} \right)^3}{N} \, dn $$

where

$$ C_{avg} = \text{Fractional conversion of } U_3O_8 $$

$$ r = \text{Particle radius} $$

$$ n = \text{Number of particles of given radius} $$

$$ N = \text{Total number of particles} $$

Although the distribution is not known, an indication of the result is given
by taking a reasonable value for the mass weighted particle size. This
would give

$$ C_{avg} = 1 - \left( \frac{r_0 - 1.94}{r_0} \right)^3 $$

where $r_0 = \text{mass average initial } U_3O_8 \text{ particle radius}$. This relationship
is shown in Figure 2.

Figure 2 alone is sufficient to demonstrate the lack of sufficient speed
of the x-ray system, providing confirmation of the chemical analyses applied.
In all runs above approximately 1600°-1700° F, the $U_3O_8$ peak was extinguished
by the time at which the temperature equilibrated. The largest particles
in the dispersion were approximately 60-65 microns in diameter as measured from micrographs. From the appearance of the dispersion, the mean particle diameter appeared to be approximately 30-40 microns or less. From Figure 2, this is seen to represent at least 27 per cent, and probably about 35 per cent, conversion of the U\textsubscript{3}O\textsubscript{8} to UO\textsubscript{2} prior to equilibration. Since the conversion to UO\textsubscript{2} yields approximately half of the total maximum estimated reaction energy, this corresponds in energy yield to the total conversion of at least 14 per cent and probably about 18 per cent of the U\textsubscript{3}O\textsubscript{8}, somewhat in excess of the established 3 per cent reaction criterion.

Although the x-ray method proved incapable of following the early stages of the Al-U\textsubscript{3}O\textsubscript{8} reaction, the data from the runs made can still be reduced to give some information about the reaction following thermal equilibration. In order to provide this information, certain assumptions are necessary. Had the speed of the x-ray system been adequate, the investigation would have included studies which would have made these assumptions unnecessary. Since the x-ray method was inadequate, however, these studies were eliminated to conserve funds for other attempts to follow the early stages of reaction. The assumptions necessitated by the abbreviated study follow:

1. The UO\textsubscript{2} diffraction peak reaches a maximum as the layer of UO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} increases in thickness and the U\textsubscript{3}O\textsubscript{8} peak is extinguished. Following this point, the UO\textsubscript{2} peak is decreased as the surface UO\textsubscript{2} is reduced according to Equation 4. As long as the UO\textsubscript{2} layer penetrates the U\textsubscript{3}O\textsubscript{8} core at a rate equal to or in excess of the UO\textsubscript{2} reduction rate, the x-ray trace will show only the effects of a reduction in the volume per cent of UO\textsubscript{2} in the
Figure 2. $\text{U}_3\text{O}_8$ Conversion to $\text{UO}_2$ at $\text{UO}_2$ X-ray Extinction.
dispersion. This condition must have been met in practice since the $U_3O_8$ peak never reappeared following its first disappearance.

2. The $UO_2$ diffraction peak area at the termination of the run is proportional to the volume fraction of the dispersion occupied by $UO_2$ and the residual $U_3O_8$ which it covers and shields. The ratio of the corrected peak area at thermal equilibration to that at termination of the run should be the same as the ratio of the $UO_2$ volume fractions at the two points. In turn, the $UO_2$ ratio should be proportional to the ratio of the $U_3O_8$ not reduced to U-Al solution. These assumptions necessitate the further assumption that there is no change in the bulk density of the $UO_2-Al_2O_3$ layer during the run.

Under these assumptions, the x-ray data can be reduced to a plot of the residual equivalent $U_3O_8$ not reduced to U-Al solution, as is shown in Figure 3. Since the $U_3O_8$ peak never reappeared after first being extinguished, the thickness of the $UO_2-Al_2O_3$ layer must have been no less at any point in the run than it was when the $U_3O_8$ peak was extinguished. Beyond this, the x-ray runs furnish no further reliable information concerning the reduction to $UO_2$.

The results summarized in Table III A and the curves of Figure 3 indicate a rapid initial reaction followed by a marked decrease in the reduction rate. This is not qualitatively inconsistent with the expected reaction mechanism although the results are quantitatively inconsistent. A consideration of the possible reaction mechanisms indicates that the following is not improbable
although it has not been verified:

1. As the reaction starts, a conversion of $\text{U}_3\text{O}_8$ to $\text{UO}_2$ occurs, forming a reaction barrier of $\text{Al}_2\text{O}_3$ and $\text{UO}_2$. This behavior was indicated by optical micrographs of partially reacted ATR dispersion and was concretely demonstrated in other Al-$\text{U}_3\text{O}_8$ dispersions. The formation of this barrier layer is relatively rapid as indicated by the x-ray studies. The solid products of Reaction 3 occupy 12 per cent less volume than the reduced $\text{U}_3\text{O}_8$.

2. Accompanying the formation of the barrier layer, some of the $\text{UO}_2$ is further reduced according to Equation 4. The only solid reaction product is $\text{Al}_2\text{O}_3$ since essentially complete reaction would be required to bring the alloy matrix across the liquidus line and into the two phase region containing $\text{UA}_3$. The $\text{Al}_2\text{O}_3$ occupies 33 per cent less volume than the original $\text{U}_3\text{O}_8$ from which it is ultimately produced.

3. The effects of temperature on the post-equilibration reaction rate are rather small in the temperature range of interest. This implies, but does not prove conclusively, that the reaction rate is not controlled by the kinetics of the Al-$\text{U}_3\text{O}_8$ reaction per se but by the rate at which aluminum can move to the reaction zone. Since volume reductions of 12 and 21 per cent, respectively, accompany Equations 3 and 4, the reaction product structure should be a porous mass of fine particles.
Figure 3. Reduction of $\text{U}_3\text{O}_8$ as a Function of Time.
The aluminum movement would thus be expected to be by bulk flow through the channels rather than by diffusion through the solids. This indicates that the reaction might be expected to proceed in the following steps:

a. Initially rapid formation of fine UO$_2$ and Al$_2$O$_3$.

b. Retardation of the UO$_2$ formation rate as the thickness of the reaction product layer increases, increasing the path length for bulk flow of the aluminum to the unreacted U$_3$O$_8$ core.

c. Concomitant reduction of the UO$_2$ according to Equation 4.

Since step c will increase the open channel area to approximately twice that made available by the reduction of U$_3$O$_8$ to UO$_2$, the resistance to flow presented by the outer layer of Al$_2$O$_3$, resulting from Equation 4, would be small compared with that presented by the inner layer of UO$_2$ and Al$_2$O$_3$. Consequently, the reduction of U$_3$O$_8$ to UO$_2$ should approach a rate determined by the rate at which the UO$_2$-Al$_2$O$_3$ barrier is removed by further reduction. This will result in a proportionality between the rates of Equations 3 and 4 following the initial unsteady state period. In addition, if the UO$_2$ formed is of very fine particle size, as is expected, its reduction will approach the conditions of a homogeneous reaction instead of a geometry controlled heterogeneous reaction. The rate of
Equation 4 should then approach first order kinetics, the rate at which the flow channel area forms should approach a constant value, and the $\text{UO}_2-\text{Al}_2\text{O}_3$ barrier should move into the $\text{U}_3\text{O}_8$ core at a constant rate, i.e., the rate of Equation 3 should be that of a surface area dependent reaction.

Under these circumstances, until the reaction is extensive enough to remove an appreciable fraction of the fine $\text{U}_3\text{O}_8$ particles, the $\text{U}_3\text{O}_8$ should follow the relation,

$$M = M_0 - \frac{4}{3} \pi \rho (r_0 - k_1 t)^3$$

(6)

where $M = \text{mass of } \text{U}_3\text{O}_8$

$M_0 = \text{original mass of } \text{U}_3\text{O}_8$

$\rho = \text{density of } \text{U}_3\text{O}_8$

$r_0 = \text{original particle radius}$

$k_1 = \text{constant}$

$t = \text{time. The reaction rate should decrease according to the equation.}$

$$R = \Delta^{2/3} R_0$$

(7)

where $R = \text{rate of } \text{U}_3\text{O}_8 \text{ conversion}$

$\Delta = \text{fraction of } \text{U}_3\text{O}_8 \text{ remaining}$

$R_0 = \text{initial rate of } \text{U}_3\text{O}_8 \text{ conversion.}$

Equation 7 predicts that the curve of $\text{U}_3\text{O}_8$ not converted to U-Al soln. during the steady state period should be a retarded cubic function of time. The data appeared to follow a linear variation moderately well. Equation 7,
however, shows that the slope of the curve will decrease from its initial value by only about 10 per cent for each 10 per cent increment in $U_3O_8$ conversion. This fact coupled with the small number of samples run would be sufficient to mask the expected form of the curve.

The x-ray curves of Figure 3 were used to estimate the steady state reaction rates and equilibration reactions during heating. These results are given in Table II.

TABLE II

REDUCTION OF $U_3O_8$ TO U-AL SOLUTION IN X-RAY TESTS

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Reaction at Temperature Equilibration $r_o = 20\mu$</th>
<th>Reaction at Temperature Equilibration $r_o = 15\mu$</th>
<th>Post-Equilibration Reaction Rate ($U_3O_8$/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(% $U_3O_8$)</td>
<td>(% $U_3O_8$)</td>
<td>(% $U_3O_8$)</td>
</tr>
<tr>
<td>1600</td>
<td>15</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>1600</td>
<td>19</td>
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<tr>
<td>2000</td>
<td>64</td>
<td>62</td>
<td>63</td>
</tr>
</tbody>
</table>

$^1$See Appendix B for details of calculation.
Several samples were heated to the various testing temperatures in the x-ray furnace and immediately cooled by shutting off the furnace power. Since the furnace is water cooled, the temperature decreased rapidly, falling below 1400° F in about 30 seconds. These samples were then analyzed chemically using the method of Appendix A in an attempt to determine the extent of the equilibration reaction. The results are shown in Table III.

### Table III

**Equilibration Reaction in X-Ray Furnace Determined by Chemical Analysis**

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>U₃O₈ Reduced To UO₂ (%)</th>
<th>To U-Al Soln (%)</th>
<th>Average U₃O₈ Reduction To UO₂ (%)</th>
<th>To U-Al Soln (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1650</td>
<td>21.4</td>
<td>5.5</td>
<td>17.4</td>
<td>2.3</td>
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<td>1650</td>
<td>13.4</td>
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<tr>
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<td>0</td>
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<td>1850</td>
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<td>1850</td>
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<td>35.6</td>
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<tr>
<td>2000</td>
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The results in Table III are obviously inconsistent. The lack of agreement, as discussed in Section 4d, is probably due to the unfavorable circumstances surrounding the chemical analysis applied. A second brief study was carried out in the last month of the program when better weighing facilities became available. The samples were heated in the x-ray furnace as described above and the method of chemical analysis described in Appendix A was used. The results of this study, as shown in Table III A, were much more consistent 1/.

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1/ Following completion of this report, similar tasks were made using a 41 w/o U3O8 dispersion. The results of this study are reported in Appendix F.
TABLE III A
EQUILIBRATION REACTION IN X-RAY FURNACE
DETERMINED BY CHEMICAL ANALYSIS USING MICROBALANCE

<table>
<thead>
<tr>
<th>Terminal Temperature (°F)</th>
<th>U₃O₈ Reduced To UO₂ (%)</th>
<th>To U-Al soln. (%)</th>
<th>Average To UO₂ (%)</th>
<th>Average To U-Al soln. (%)</th>
<th>Heating Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>66.8</td>
<td>5.5</td>
<td>63.6</td>
<td>3.0 (6.8²)</td>
<td>97</td>
</tr>
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<td>+5.2²</td>
<td>+6.6</td>
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<tr>
<td>1800</td>
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<td>-2.6⁴</td>
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<td>65.9</td>
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<td>+1.7</td>
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<tr>
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<td></td>
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<td>8.1</td>
<td></td>
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<tr>
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<td>47.1</td>
<td>16.2</td>
<td>64.8</td>
<td>12.8</td>
<td>151</td>
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<tr>
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<td>+3.0</td>
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<td>1950</td>
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<td>14.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1950</td>
<td>78.8</td>
<td>10.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹Specimens showed residue content after firing greater than average residue content of unfired plate.

²Average without specimens marked superscript 1.

³Range of the mean at the 95 per cent level of confidence.

⁴Time to reach peak temperature after 1300° F attained.
The data of Table III A are sufficiently consistent to warrant statistical analysis. The results of the analysis, given in Appendix D, show that neither the UO₂ analyses nor the 1900° and 1950° F U-Al solution analyses differ significantly. The 1800° F U-Al solution analysis is significantly lower than those for the other temperatures.

3. Quenching Studies

In an attempt to provide data for the initial stages of the U₃O₈ reduction reaction, a DTA furnace was modified to permit rapid heating specimens. The specimen was held in the water-cooled observation port of the furnace by a ferrous grid and an external magnet. The specimen was shielded from the furnace chamber by a piece of aluminum foil. Although the aluminum foil was molten by the time the furnace reached temperature, the surface oxide film was strong enough to support its weight and keep it intact. When the magnet was removed, the specimen fell through the aluminum foil into the furnace. After a predetermined time, the top of the furnace was removed and the silica hearth and specimen were quenched in liquid nitrogen. After cooling, the specimens were analyzed for U₃O₈ conversion by the iodine-methanol method of Appendix A.

The heating curve for the specimens was approximated since direct measurement for the rapidly heated specimens was impractical. A thermocouple was spot welded to a specimen held in the observation port and shielded by aluminum foil as in the quenching runs. The specimen was pushed through the foil mechanically and the temperature was recorded. The heating curve of the quenched specimens is shown in Figure 4 with
The results of the quenching studies are given in Table IV.

**TABLE IV**

**RESULTS OF QUENCHING RUNS**

<table>
<thead>
<tr>
<th>Heating Time (sec)</th>
<th>Approximate Terminal Temperature (°F)</th>
<th>U₃O₈ Reduction</th>
<th>Average U₃O₈ Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>To UO₂ (%)</td>
<td>To U-Al Soln (%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(%)</td>
<td>(%)</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>1680</td>
<td>47.5</td>
<td>16.9</td>
</tr>
<tr>
<td>18</td>
<td>1680</td>
<td>0</td>
<td>9.9</td>
</tr>
<tr>
<td>18</td>
<td>1680</td>
<td>0</td>
<td>13.4</td>
</tr>
<tr>
<td>38</td>
<td>1850</td>
<td>85.1</td>
<td>17.5</td>
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<td>38</td>
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<td>7.8</td>
</tr>
<tr>
<td>78</td>
<td>1950</td>
<td>0</td>
<td>9.8</td>
</tr>
<tr>
<td>78</td>
<td>1950</td>
<td>67.7</td>
<td>11.1</td>
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<td>138</td>
<td>2000</td>
<td>0</td>
<td>13.8</td>
</tr>
<tr>
<td>138</td>
<td>2000</td>
<td>44.1</td>
<td>17.7</td>
</tr>
</tbody>
</table>

¹Time to peak temperature after 1300°F reached.

4. Discussion and Conclusions

On examination of the results of the various studies, it is evident that no single technique yielded data accurate enough to stand alone. The strength and utility of the investigation emanates from a composite of all the results obtained. The reasonable agreement among the different techniques reinforces the apparent reliability of conclusions to be drawn from this composite. The
Figure 4. Heating Curves above 1300°F for Quenching, X-ray and DTA Runs.
information revealed by each of the studies and the conclusions drawn from the composite data are discussed below.

a. DTA Studies. The extent of the thermal differential during an exothermic reaction will be regulated by two factors, the rate of energy evolution by the reaction and the rate of heat transfer from the pellet. If the heating rate is high, the reaction will occur at a higher mean temperature and, if the reaction shows the normal temperature dependence, the rate of energy evolution is high and a larger exotherm peak results. If the reaction is rapid, a substantial exotherm is observed while a slow reaction may produce no observable exotherm at all. In the same manner, if the pellet is a good conductor of heat, a more rapid reaction will be required to produce a given exotherm than in a pellet of poor conductivity.

In the analysis of the ATR dispersion, only a rapid reaction will produce a noticeable exotherm since the pellet does possess excellent heat transfer capabilities. A reasonable argument thus seems to be that the exotherms of Figure 1 represent only the initial rapid reaction during which the UO$_2$ - Al$_2$O$_3$ barrier layer forms according to Equation 3. The subsequent slower reaction shown by the x-ray curves of Figure 3 is probably sufficiently slow not to cause a substantial thermal differential to occur. Any reduction of the UO$_2$ to U-Al solution which accompanies the formation of the barrier layer will also be included in the peak. As a result, the DTA exotherm should represent the total energy release corresponding to the equilibration reaction.
The major sources of error, as previously discussed, are the difficulty of selection of a base line and the assumption of constant heat transfer characteristics above the melting point of aluminum. The heat transfer characteristics should not change noticeably in the temperature range of interest since the principal influence would be expected to be that of geometry and specimen orientation. Inasmuch as the pellet geometry and orientation are the same during the aluminum endotherm and the reaction exotherm this influence should be small. The base line was established by extrapolating the slope of the DTA curve before the aluminum endotherm to fix the zero differential 1/.

After completion of the reaction, the DTA trace will return to the base line characteristic of the fired pellet being run against the standard. This secondary base line is seen from the cooling curves of Figure 1 to be a straight line. Its position on the heating curve would be determined by asymptotic approach of the DTA trace following completion of the reaction. The curves of Figure 1 show that this point of asymptotic approach will lie to the right of the extrapolated base line. The true base line is thus likely to be curved, beginning below the aluminum melting point with the slope of the pre-melting DTA trace and terminating as an almost straight line at the point of asymptotic approach of the post-firing trace. The true base line thus appears likely to be a curve, concave to the right and lying wholly to the right of the extrapolated base line. As a result, the procedure used in estimating energy evolution from the DTA

1/See Figure 1 for typical extrapolation.
curves should yield values which are too low. In addition, low results should be produced by any intrinsic errors in the method such as departure of the unknown from adiabatic conditions due to radiation during the reaction.

The major value of the energy estimate from the DTA test lies in its comparison with the values from the other tests in light of the expected deviation. Had the DTA test yielded higher values than those from the tests involving chemical analysis, serious doubts would have been cast on the credibility of the latter values. As it is, however, the DTA tests are of significant importance in that they are an entirely independent indication of the energy release which does deviate in the expected direction from the results calculated from the chemical analyses. The fact that the results from DTA and chemical analysis differ by approximately an order of magnitude is of no significance since the errors in the DTA test lead to low results, which may be quite appreciable, while the chemical analysis results were purposely manipulated to yield conservatively high calculated values. Better agreement than was obtained would be quite disturbing rather than pleasing.

b. X-ray Studies. Of all the studies made, the x-ray runs appear to be the least reliable in view of the necessity for making several assumptions and the fact that so few specimens were run. Nevertheless, the x-ray runs are generally internally consistent and comparison with the results of the other tests implies that the x-ray results tend to be too conservative, i. e., yield equilibration reactions too high. These results seem, therefore,
to be limiting on the conservative side of any energy release rate considerations.

Concerning the assumptions made, the first apparent major source of error is the assumption that the apparent volume fraction of UO₂ shows exactly the same variation with time as the equivalent U₃O₈ not reduced to U-Al solution. In effect, this assumption means that the surface UO₂-Al₂O₃ occupies the same volume as the U₃O₈ from which it formed. Since the reduction to UO₂ is accompanied by a theoretical volume decrease of 12 per cent, there is no apparent mechanism which would cause the barrier layer to occupy more volume than that of the U₃O₈ which it replaces. As a result, any deviation of the amount of U-Al solution formed from the amount of UO₂ indicated by the x-ray test to be reduced will be in the conservative direction since the U₃O₈ volume must be equal to or greater than the volume shown by the UO₂-Al₂O₃ barrier layer. The actual U₃O₈ reduction to U-Al solution must be equal to or less than that indicated by the x-ray data, within the assumption used in data reduction.

The second major source of error is in the uncertainties surrounding the influences of non-homogeneous x-ray absorption in the dispersion and absorption of the x-ray beam by the surface Al₂O₃ layer left during reduction of the UO₂ to U-Al solution and increased absorption by the alloy phase as its uranium content increases. These errors are in opposite direction and tend to cancel. The effects of these errors are discussed in Appendix B.
The equilibration conversion of \( \text{U}_3\text{O}_8 \) to U-Al solution was calculated making use of the non-homogeneity and absorption correction factors of Appendix B. The only predictable variation is that caused by uncertainty as to the initial \( \text{U}_3\text{O}_8 \) particle size. The best estimate of the particle size which can be made from micrographs, without an extensive statistical study, places the range at 30 to 40 microns. The possibility of an average size much in excess of 40 microns appears remote while a size less than 30 microns is entirely possible. Since the non-homogeneity correction predominates with decreasing particle size, the equilibration estimates at 40 and 30 microns appear conservative.

The steady state reaction rates were determined by plots of the x-ray data uncorrected for non-homogeneity and Al\(_2\)O\(_3\) absorption. The effect of these corrections is to decrease the values for unconverted \( \text{U}_3\text{O}_8 \), with the amount of decrease becoming greater at higher values of unconverted \( \text{U}_3\text{O}_8 \). Application of this correction would then tend to decrease the slopes of the x-ray curves following equilibration. The steady state reaction rates determined without correction of the x-ray data are therefore conservative.

The results of the x-ray analysis are incapable of providing direct information concerning the reduction of \( \text{U}_3\text{O}_8 \) to \( \text{UO}_2 \) since the initial reaction completely extinguished the \( \text{U}_3\text{O}_8 \) diffraction peak.
c. Quenching Studies. Little remains to be said concerning the quenching studies. Aside from the errors associated with the chemical analysis, discussed elsewhere, the only apparent source of error is the method of temperature measurement. Since the mechanics of the heating and quenching operation made monitoring of the sample temperature impossible, its estimation was required. This was accomplished by determination of the heating curves of samples heated in essentially the same manner as the quenching samples but free of the requirement of rapid removal from the furnace. The heating curves determined in this manner were used to estimate the peak temperature from the pre-set heating time. The error in this method of peak temperature determination was as much as ±75° F. Even with this large error, however, only the highest temperature runs show a possibility of overlapping and duplication. Since the results of the runs showed no significant differences in the extent of reaction, this error seems immaterial below about 1850° F.

Since the samples in the quenching study were subjected to chemical analysis, the results show both conversion of $U_3O_8$ to U-Al solution and to $UO_2$, within the accuracy of the analysis.

d. Chemical Analyses. Without question, the method of chemical analysis is the weakest link in the investigation. The inadequacy of the method is not inherent but stems from the very low $U_3O_8$ content of the reference ATR plate. Since the specimen size which could be used in the experimental systems was limited, the maximum $U_3O_8$ content of any sample
subjected to chemical analysis was 120 mg. This sample size was most unsuited to the limitations placed on the program by finances and time. Any more suitable method of analysis was prohibited by a much higher cost and greater time requirement.

The method of analysis used in this investigation would be quite suitable for samples of the same physical size if they consisted entirely of Al-$\text{U}_3\text{O}_8$ dispersion instead of only the 20 volume per cent dispersion contained in the aluminum clad ATR reference plates. Such material was not available, however, and use of the ATR plates could not be avoided.

More accurate weighing equipment has recently been purchased for use in another program. The results on Table III A obtained using this equipment are much more consistent and appear to support the reliability of the method.

In addition to the uncertainties stemming from the method of chemical analysis applied, additional errors arose from non-uniform distribution of $\text{U}_3\text{O}_8$ in the test specimens. These errors and those from the method itself are discussed further in Appendix C.

e. Reduction to U-Al Solution. Estimates of the amount of $\text{U}_3\text{O}_8$ reduced to U-Al solution during the initial rapid reaction can be made from the extrapolated x-ray data, the chemical analyses of samples heated to temperature in the x-ray furnace and immediately cooled, and chemical analyses of the samples from the quenching studies. These data are summarized in Table V.
**TABLE V**

U\(_3\)O\(_8\) REDUCTION TO U-Al SOLUTION DURING EQUILIBRATION

<table>
<thead>
<tr>
<th>Peak Temperature (°F)</th>
<th>U(_3)O(_8) Reduction to U-Al Solution</th>
<th>Chemical Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X-ray Extrapolation</td>
<td>Chemical Analysis</td>
</tr>
<tr>
<td></td>
<td>d(_0) = 40µ</td>
<td>d(_0) = 30µ</td>
</tr>
<tr>
<td>1600</td>
<td>17</td>
<td>11</td>
</tr>
<tr>
<td>1650</td>
<td>13.4</td>
<td>12</td>
</tr>
<tr>
<td>1680</td>
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<td>11</td>
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<td>1750</td>
<td>17</td>
<td>12</td>
</tr>
<tr>
<td>1800</td>
<td>28</td>
<td>18</td>
</tr>
<tr>
<td>1850</td>
<td>17</td>
<td>12</td>
</tr>
<tr>
<td>1900</td>
<td>41</td>
<td>37</td>
</tr>
<tr>
<td>1950</td>
<td>64</td>
<td>62</td>
</tr>
<tr>
<td>2000</td>
<td>17</td>
<td>11</td>
</tr>
</tbody>
</table>

\(^1\)Results from Table III.

\(^2\)Results from Table III A.
Examination of the data of Table V shows fair consistency among the different methods at temperatures below 1900°F and poor agreement at the higher temperature. Attempts to explain the differences should probably not be pressed too far in view of the small number of samples in each group and the lack of valid statistics to evaluate the reality of the variation.

The x-ray extrapolation method is based on several assumptions which are unverified. This method is also subject to the accuracy of the chemical analysis which was used to establish the end point. The error in this analysis due to nonuniform U₃O₈ content of the specimens alone is estimated to be as high as 25 per cent. The overall error, including random factors, and the fact that only one sample was run at the higher temperatures indicates that even the 64 per cent extent of reaction determined by extrapolation of the 2000°F run may not differ statistically from the results of the chemical analysis runs at 2000°F.

Only the values obtained from the samples heated in the x-ray furnace and weighed on the microbalance were reproducible enough to benefit from statistical analysis. The credibility of these results benefits from the good agreement obtained 1/. In the majority of the cases, with the only exception being at 1900°F where only one sample was run, the chemical analyses from the x-ray studies and quenching studies, obtained using the old balance, and the analyses obtained with the new microbalance agreed well.

1/Confirmation of these results by a second independent method of chemical analysis would be desirable but such was not possible within the scope of this program. Nothing, however, in the experience with the iodine-methanol analysis or in the literature serves to produce doubts as to its validity.
As a result, the chemical analysis averages, assigning equal weight to each sample, seem to be the most reasonable values for use in estimating the equilibration energy release by reduction to U-Al solution. The most conservative values, on the other hand, would be the highest points from any of the tests.

The reduction rates of $\text{U}_3\text{O}_8$ to U-Al solution following equilibration can be estimated from the x-ray data or from the chemical analyses. The rates from the x-ray analyses were obtained from the slopes of the lines in Figure 3. The rates from chemical analyses were obtained by assuming a constant rate and using the terminal chemical analyses from the x-ray runs and the averaged values for the equilibration reaction determined by chemical analyses. Except at 1700°F, the latter method yielded the higher and more conservative values for the reaction rates.

The composite values for reduction to U-Al solution, obtained as described above from all the studies, are given in Table VI. In this table, all temperatures were rounded to the nearest 50°F since the accuracy of temperature measurement was probably no more than ±20°F.
### TABLE VI

**COMPOSITE VALUES FOR U₃O₈ REDUCTION TO U-Al SOLUTION**

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Equilibration Conversion</th>
<th>Post-equilibration Reaction Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High¹</td>
<td>Low²</td>
</tr>
<tr>
<td>1600</td>
<td>13.0</td>
<td>---</td>
</tr>
<tr>
<td>1650</td>
<td>----</td>
<td>2.3</td>
</tr>
<tr>
<td>1700</td>
<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>1750</td>
<td>----</td>
<td>15.4</td>
</tr>
<tr>
<td>1800</td>
<td>15.0</td>
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<td>----</td>
<td>12.2</td>
</tr>
<tr>
<td>2000</td>
<td>63</td>
<td>11.3</td>
</tr>
</tbody>
</table>

¹From x-ray extrapolation.

²From chemical analysis.
f. Reduction to UO₂. Since the x-ray technique proved incapable of revealing the kinetics of the conversion of U₃O₈ to UO₂, all direct information concerning this reduction must be drawn from the studies involving chemical analysis. This is unfortunate since the method of chemical analysis was characterized by gross error in the UO₂ determination. The results of the studies in Table III and IV show extreme variations in the UO₂ analysis and cannot be taken to have any accuracy whatever, standing alone. Table III A shows consistent results for the UO₂ formation during equilibration and these values must be assumed accurate since they were not controverted by any of the other experiments.

While no additional experimental data were obtained, other observations tend to indicate that the UO₂ values of Table III A are conservative. Metallographic examination of the reacted specimens furnished concrete proof that the reduction to UO₂ is not complete during the early rapid reaction. Even in samples heated to 2000° F, a considerable quantity of U₃O₈ was seen. This is supported by x-ray diffraction. A sample heated to 2000° F and cooled immediately shows no U₃O₈ diffraction peaks as a result of complete extinction by the UO₂ surface layer. If the surface of the same sample is lightly ground, however, and again examined by x-ray diffraction, strong U₃O₈ peaks are again obtained although a UO₂ peak of diminished intensity does remain. Unfortunately, the sample cannot be realigned in the same exact manner after grinding as it was before. The method thus provides no quantitative determination of the residual U₃O₈. The peak areas do indicate,
however, that a substantial quantity of $U_3O_8$ remains unreacted. The best estimate of residual $U_3O_8$ that can be made from either metallography or pre- and post-grinding x-ray diffraction is that about half of the $U_3O_8$ remains. In addition to limiting the amount of $U_3O_8$ reduced to $UO_2$ during equilibration, this confirms the earlier suggestion that the $2000^\circ F$ x-ray test result for conversion of $U_3O_8$ to U-Al solution is conservative.

The only additional quantitative estimate of the reduction to $UO_2$ during the early reaction is furnished by the observations of extinction of the $U_3O_8$ diffraction peak during the x-ray tests. The amount of $U_3O_8$ conversion to $UO_2$ required to bring about this extinction was estimated from absorption calculations to be 27 to 35 per cent as seen from Figure 2. Since extinction of the $U_3O_8$ peak occurred at approximately the time of temperature equilibration in all runs, with the possible exception of the $2000^\circ F$ run, this implies that the $U_3O_8$ conversion to $UO_2$ during equilibration was approximately 27 to 35 per cent at all temperatures. This lack of temperature dependence of the reduction to $UO_2$, also noted in the results of Table III A, is not illogical since this reaction must proceed by aluminum permeation to the unreacted $U_3O_8$ core. The only effect of temperature would be through a decrease in the viscosity of aluminum if the permeation is the rate controlling process rather than the chemical kinetics of the reduction at the $U_3O_8$ core surface. This would be expected to produce a much lower temperature dependence than if the reduction kinetics did control.

By this same argument, it is difficult to see how the rate of reduction of $U_3O_8$ to $UO_2$ past the equilibration point could exceed, by any substantial
amount, the rate of reduction of UO₂ to U-Al solution. The initially rapid reaction is likely to be limited by the build-up of the Al₂O₃-UO₂ barrier layer which must reduce the rate of aluminum penetration to the U₃O₈ core. Once the early rapid reaction subsides, further production of UO₂ at the U₃O₈ core surface should depend principally on the rate at which the permeation-retarding barrier is removed by further reduction of the UO₂ to U-Al solution. As a result, although no experimental evidence whatever is available, it appears safe to conclude that the rate of U₃O₈ reduction to UO₂ must be equal to or less than the rate of reduction to U-Al solution. The reaction rates of Table VI should then be fair estimates of the rates of reduction of U₃O₈ to UO₂.

Composite values, drawn from all studies, are given for the reduction of U₃O₈ to UO₂ in Table VII. As before, the temperatures were rounded to the nearest 50°F. At the lower temperatures the low values for the equilibration reaction were obtained from the chemical analyses and the high values are the U₃O₈ x-ray peak extinction results. The intermediate temperature results showed lower values for the x-ray extinction. Above 1800°F, the chemical analysis results obtained using the old balance were discarded in favor of those obtained with the new balance and the extinction results were generally lower than the chemical analysis results.
## TABLE VII

**COMPOSITE VALUES FOR U\textsubscript{3}O\textsubscript{8} REDUCTION TO UO\textsubscript{2}**

<table>
<thead>
<tr>
<th>Temperature (°)</th>
<th>Equilibration Conversion</th>
<th>Post-Equilibration Reaction Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>(% U\textsubscript{3}O\textsubscript{8})</td>
<td>(% U\textsubscript{3}O\textsubscript{8})</td>
</tr>
<tr>
<td>1600</td>
<td>31</td>
<td>---</td>
</tr>
<tr>
<td>1650</td>
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</tr>
<tr>
<td>2000</td>
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<td>22.4</td>
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</tbody>
</table>
g. Estimates of Energy Release. In converting the reduction parameters to energy release data, several factors come into play. If the diffusion of uranium in molten aluminum is low, the alloy phase composition after reaction occurs can be determined by considering the uranium formed to remain in the region occupied by the fuel meat. The percentage reduction of $U_3O_8$ to take the alloy outside the liquid region and into the liquid plus $UA_3$ region is given in Table VIII along with the actual equilibration reduction determined in the study. A comparison of these values shows that in no case does the early rapid reaction bring the alloy phase into the region containing $UA_3$. If the diffusivity of uranium in aluminum is high, the reduced uranium will be diluted by the cladding and the ATR clad plate cannot enter the region containing $UA_3$ under any circumstances. Total reduction of the $U_3O_8$ to free uranium would then follow the equation

$$U_3O_8 + x's Al \rightarrow U-Al_{(soln)} + \frac{8}{3} Al_2O_3.$$  \hspace{1cm} \text{Equation 8}$$

Equation 8 is balanced with respect to oxygen only since the aluminum is present in excess. The heat of reaction for Equation 8 is given by

$$\Delta h_R = \frac{8}{3} \Delta h_f (Al_2O_3) + \Delta h_s (U-Al) - \Delta h_f (U_3O_8)$$  \hspace{1cm} \text{Equation 9}$$

where $\Delta h_s (U-Al)$ represents the heat of solution of uranium in aluminum at the appropriate dilution. This heat of solution is not known, but it is probably relatively small. Certainly the heat of solution would be much less than the heat of formation of $UA_4$. Taking this heat of solution as
zero and as the heat of formation of UA1₄ extrapolated to the temperature of interest establishes the range of maximum energy release given in Table IX.

**TABLE VIII**

U₃O₈ REDUCTION TO FORM SOLID UA1₃

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Reduction Required (%) U₃O₈</th>
<th>Highest Estimated Equilibration Reduction (%) U₃O₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>66</td>
<td>13</td>
</tr>
<tr>
<td>1700</td>
<td>76</td>
<td>13</td>
</tr>
<tr>
<td>1800</td>
<td>86</td>
<td>15</td>
</tr>
<tr>
<td>1900</td>
<td>100</td>
<td>31</td>
</tr>
<tr>
<td>2000</td>
<td>100</td>
<td>63</td>
</tr>
</tbody>
</table>
TABLE IX
ENERGY RELEASE IN REDUCTION OF U₃O₈ IN ATR REFERENCE PLATE

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Reduction to UO₂ (kcal/kg U₃O₈)</th>
<th>Reduction to U-Al Solution</th>
<th>Minimum (kcal/kg U₃O₈)</th>
<th>Maximum (kcal/kg U₃O₈)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>229.5</td>
<td></td>
<td>264.6</td>
<td>442.4</td>
</tr>
<tr>
<td>1650</td>
<td>229.5</td>
<td></td>
<td>264.6</td>
<td>443.2</td>
</tr>
<tr>
<td>1700</td>
<td>229.4</td>
<td></td>
<td>264.5</td>
<td>443.9</td>
</tr>
<tr>
<td>1750</td>
<td>229.2</td>
<td></td>
<td>264.5</td>
<td>444.6</td>
</tr>
<tr>
<td>1800</td>
<td>229.0</td>
<td></td>
<td>264.5</td>
<td>445.2</td>
</tr>
<tr>
<td>1850</td>
<td>228.9</td>
<td></td>
<td>264.5</td>
<td>445.9</td>
</tr>
<tr>
<td>1900</td>
<td>228.8</td>
<td></td>
<td>264.5</td>
<td>446.6</td>
</tr>
<tr>
<td>1950</td>
<td>228.7</td>
<td></td>
<td>264.5</td>
<td>447.2</td>
</tr>
<tr>
<td>2000</td>
<td>228.6</td>
<td></td>
<td>264.5</td>
<td>447.7</td>
</tr>
</tbody>
</table>
If the heat of solution of uranium in aluminum is zero, additional energy, above the release by the reduction of the U₃O₈, will be released during cooling of the reacted plate. If the diffusivity of uranium in aluminum is high, this release in the clad plate will be governed by the cooling characteristics of a 7.6 per cent uranium alloy when the U₃O₈ reduction is 100 per cent. If the diffusivity is low, the release will follow the cooling characteristics of a 34.5 per cent uranium alloy for reduction of all of the U₃O₈. Intermediate diffusivity will produce cooling characteristics intermediate between the two limiting conditions while fractional reduction of the U₃O₈ will produce a similar cooling behavior but with lower energy release. The cooling energy release does not include the release during solidification of the excess aluminum.

**TABLE X**

COOLING ENERGY RELEASE IN COMPLETELY REACTED ATR REFERENCE PLATE

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Process</th>
<th>Poor U-Al Diffusivity (kcal/kg U₃O₈)</th>
<th>Good U-Al Diffusivity (kcal/kg U₃O₈)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1870 - 1380</td>
<td>UAl₃ Formation</td>
<td></td>
<td>94.0</td>
</tr>
<tr>
<td>1380</td>
<td>UAl₃ Conversion to UAl₄</td>
<td></td>
<td>32.6</td>
</tr>
<tr>
<td>1380 - 1184</td>
<td>UAl₄ Formation</td>
<td>129.4</td>
<td>29.5</td>
</tr>
<tr>
<td>1184</td>
<td>UAl₄ Formation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Cooling Energy Release</td>
<td></td>
<td>129.4</td>
<td>170.0</td>
</tr>
</tbody>
</table>
If the heat of solution of uranium in aluminum is equal to the heat of formation of UA\(_{14}\), no energy release will occur during cooling since formation of UA\(_{14}\) from the solution would have a heat of reaction equal to zero and formulation of UA\(_{3}\) would be endothermic. Intermediate heats of solution would give the same pattern of cooling energy release but a lower amount of energy.

Based on this discussion of the system thermochemistry, calculations were made of estimated values for energy release during reduction in ATR reference plates. The reduction parameters used in this calculation were selected from Tables VI and VII. In view of the dubious results in most of the studies, conservative selections of the amount of U\(_3\)O\(_8\) reduction were made according to the following rules:

1. The high values were used.

2. If the high value was less than that at a lower temperature, the lower temperature value was used.

3. If no value was available at a given temperature, that for the next higher temperature was used 1/.

4. If the sum of the conversion to UO\(_2\) and to U-Al solution exceeded 100 per cent, the high UO\(_2\) value was used and the conversion to U-Al solution was set equal to 100 minus the conversion to UO\(_2\).

---

1/No value was available for the conversion to UO\(_2\) at 2000\(^\circ\) F. Since the results at 1800\(^\circ\), 1900\(^\circ\), and 1950\(^\circ\) agreed well, a value of 66 per cent was used for 2000\(^\circ\) F.
The energy release values were calculated by adding the products of the reduction parameters from Tables VI and VII and the appropriate energies from Table IX 1/. The results are given in Table XI. Use of the lower energy release figures is recommended since the heat of solution of uranium in aluminum is probably small.

**TABLE XI**

**ESTIMATED ENERGY RELEASED BY REDUCTION OF ATR REFERENCE PLATE**

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Equilibration Reduction</th>
<th>Highest Post-Equilibration Release Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum (kcal/kg U₃O₈)</td>
<td>Minimum (kcal/kg U₃O₈)</td>
</tr>
<tr>
<td>1600</td>
<td>129</td>
<td>106</td>
</tr>
<tr>
<td>1650</td>
<td>129</td>
<td>106</td>
</tr>
<tr>
<td>1700</td>
<td>129</td>
<td>105</td>
</tr>
<tr>
<td>1750</td>
<td>138</td>
<td>111</td>
</tr>
<tr>
<td>1800</td>
<td>215</td>
<td>187</td>
</tr>
<tr>
<td>1850</td>
<td>289</td>
<td>233</td>
</tr>
<tr>
<td>1900</td>
<td>289</td>
<td>233</td>
</tr>
<tr>
<td>1950</td>
<td>303</td>
<td>241</td>
</tr>
<tr>
<td>2000</td>
<td>303</td>
<td>241</td>
</tr>
</tbody>
</table>

1/See Appendix E for sample calculation.
B. Strength of Molten Al-\(\text{U}_2\text{O}_8\) Dispersions

Attempts were made to provide rough indications of the load-bearing capability of Al-3\(\frac{1}{4}\) w/o \(\text{U}_2\text{O}_8\) composites at elevated temperatures. A vertical 1/4-inch outside diameter tube was passed through the floor of a DTA furnace. A specimen, 1/2-inch square by approximately 90 mils thick, was placed over the open end of the tube. The tube was valved through a manometer to the inside of the furnace and provisions were made to draw a controlled vacuum on the tube. Since, as melting occurred, the specimen sealed the tube, a controlled pressure differential could be established between the slightly evacuated tube and the body of the furnace at 16 psi of argon. Following temperature equilibration, the pressure differential was produced and increased slowly until the sample could be seen to sag. In some cases, the specimen went on to rupture as soon as sag occurred. In others, the sag plugged the tube and no further deformation was obtained. The results of this sag test are summarized in Table XII.
TABLE XII
PRESSURE DIFFERENTIAL REQUIRED TO PRODUCE SAG IN Al-U₃O₈ COMPOSITES

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Testing Temperature (°F)</th>
<th>Specimen Thickness (mils)</th>
<th>Pressure Differential Required to Produce Sag (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>1350</td>
<td>93</td>
<td>1.1</td>
</tr>
<tr>
<td>15</td>
<td>1380</td>
<td>93</td>
<td>0.6</td>
</tr>
<tr>
<td>16</td>
<td>1360</td>
<td>90</td>
<td>1.4</td>
</tr>
<tr>
<td>17</td>
<td>1350</td>
<td>85</td>
<td>0.6</td>
</tr>
<tr>
<td>18</td>
<td>1700</td>
<td>95</td>
<td>0.7</td>
</tr>
<tr>
<td>19</td>
<td>1710</td>
<td>90</td>
<td>0.9</td>
</tr>
<tr>
<td>20</td>
<td>1710</td>
<td>90</td>
<td>0.9</td>
</tr>
<tr>
<td>21</td>
<td>1860¹</td>
<td>90</td>
<td>&gt;4²</td>
</tr>
<tr>
<td>22</td>
<td>1860¹</td>
<td>85</td>
<td>&gt;4²</td>
</tr>
</tbody>
</table>

¹ Specimens permitted to fire prior to application of pressure differential.
² Maximum pressure obtainable in apparatus.

While it is obvious that the data of Table XII are not conclusive or accurate, and that they were obtained from specially rolled material rather than reference plates, they appear uniform enough to confirm that the unreacted Al-U₃O₈ composites do possess some strength even when molten. The strength does not decrease much, if at all, in the temperature range between melting and rapid reaction. In addition, the reacted specimens are substantially stronger at temperature than unreacted specimens.
Preliminary metallography of the sag specimens indicated rather peculiar behavior. A typical specimen is illustrated in Figure 5. The macrograph shows that the displaced mass of material is apparently almost free of oxide. This observation is confirmed by the micrographs which show that the exuding material left the oxide behind.

The implications of the macro- and micrographs are most interesting. The apparent exfiltration of the oxide-free aluminum may indicate that the U₃O₈ is linked in a continuous network, possibly of Al₂O₃, and/or stringered U₃O₈. Failure of the specimen under a pressure differential could proceed by collapse of this network after exfiltration of a significant amount of aluminum. The presence of such an oxide network could account for the failure of the specimens to weaken significantly with increasing temperature. In addition, reinforcement of the oxide network upon Al-U₃O₈ reaction could account for the substantial increase in strength at temperature following reaction.

If an oxide network does exist in the Al-U₃O₈ specimens, some consideration must be given to the effects of loading rate on the strength at temperature. Rapid load application might produce a higher temporary strength since the aluminum would not have time to "exude" and weaken the structure. If the load-bearing capacity of the Al-U₃O₈ dispersion is of design importance in its use as a fuel, a need for more detailed studies may be indicated.
(a) Al–U₃O₈ Dispersion Sag Tested at 1380°F (7x)

(b) Etched in 0.5% HF (250x)

(c) Etched in 0.5% HF (250x)

Figure 5. Al–U₃O₈ Dispersion Sag Tested at 1380°F.
IV. CONCLUSIONS

The results of this program lead to the following conclusions:

1. The Al-U$_3$O$_8$ reaction proceeds slowly at temperatures below about 1600° F and rapidly between 1700° and 1800° F.

2. The reaction proceeds in two steps, initial reduction to UO$_2$ and subsequent reduction of the UO$_2$ to U-Al solution.

3. During the initial stages of reaction, approximately 65 per cent of the U$_3$O$_8$ is reduced to UO$_2$ and approximately 15 per cent is reduced to U-Al solution. The rate of this initial reaction is too rapid to be determined by the techniques employed in this program.

4. During the early rapid reaction, the total energy release is approximately 100 to 200 kcal per kg. of U$_3$O$_8$. Since most of this energy is released in the temperature range of 1700°-1800° F, the corresponding energy release rate is at least 1 to 2 kcal per second. Inasmuch as the reaction rate decreases with time, the maximum energy release rate is probably somewhat larger than this average rate.

5. Following the initial rapid reaction, further reduction of the U$_3$O$_8$ proceeds much more slowly at a maximum rate of approximately 2 per cent per minute at 1700° F and 8 per cent per minute at 2000° F. The corresponding energy release rate is estimated to be 10 to 40 kcal per minute per kg. of U$_3$O$_8$. 
6. No statistically significant differences exist in the extent of rapid initial $U_3O_8$ reduction in 34 and 41 w/o $U_3O_8$ dispersions. This conclusion is based on a limited number of tests.

7. Al-$U_3O_8$ dispersions retain some strength above the melting point of aluminum. This strength increases by better than a factor of four after completion of the Al-$U_3O_8$ reaction. Deformation prior to the reaction occurs by exudation of oxide-free alloy from the dispersion.

V. PERSONNEL

The work discussed in this report was conducted in the High Temperature Materials Branch, Mr. J. D. Walton, Head. The project was directed by Dr. J. D. Fleming with Mr. J. W. Johnson acting as Assistant Project Director. Major contributing personnel were:

- Mr. S. H. Bomar
  - Group Leader
- Mr. N. K. Hearn
  - Assistant Research Physicist
- Mr. P. A. Darius
  - Technician
- Mr. A. C. Evans
  - Technician
- Mr. E. W. Hearn
  - Technician
APPENDIX A

METHOD OF CHEMICAL ANALYSIS

The analytical technique employed in the program was based on a method developed by Argonne National Laboratory 1/. It involves digestion of the sample in a solution of approximately 7.5 gm. of iodine per 100 ml. of methanol. The digestion is carried out overnight at 150° F using approximately 300 cc. of solution per gram of sample. During digestion, the aluminum and uranium-aluminum intermetallic compounds are dissolved, leaving behind the oxides of aluminum and uranium. The undissolved residue is filtered, dried, and weighed. Following this step, the residue is heated for one hour at 900° F in air to convert any UO₂ present to U₃O₈, cooled and reweighed.

If the original amount of undissolved residue in the unheated specimen is known, as determined from blank analyses using unheated specimens, the dried residue weight following digestion and the oxidation weight gain can be employed to determine the percentage of U₃O₈ converted to U-Al solution and to UO₂. The pertinent equations determined by material balances based on Equations 3 and 4 are

\[
\% \text{ U}_3\text{O}_8 \text{ reduced to U-Al solution} = \frac{147.7 (R-D) + 167W}{R} \quad \text{A-1)}
\]

and

\[
\% \text{ U}_3\text{O}_8 \text{ reduced to UO}_2 = \frac{2630 W}{R} \quad \text{A-2)}
\]

1/Private communication from Dr. Louis Baker.
Final Report, Project No. B-153, Task II

where

\[ R = \text{undissolved residue per gram of sample in unheated specimen} \]

\[ D = \text{undissolved residue per gram of sample in heated specimen} \]

\[ W = \text{oxidation weight gain per gram of sample}. \]
In reducing the results of the x-ray tests to usable information, many doubts arise as to the necessary corrections to be applied. Most of these corrections would have been unnecessary had the full experimental program been possible. Under the circumstances, however, consideration of these corrections is essential even if their application is precluded for practical reasons.

Most of the corrections arise from two sources, absorption of the beam diffracted by the \( \text{UO}_2 \) and non-homogeneous diffraction as a result of the coarsely particulate \( \text{U}_3\text{O}_8 \). Fortunately, the corrections seem to be qualitatively compensating although the quantitative extent of compensation cannot even be estimated with any degree of confidence. Most of the corrections are too complex to permit application with convenience and even the methods to be used could not be determined without an extensive secondary investigation. In particular, absorption by the U-Al matrix solution would certainly be important but its correction would involve an extremely tedious trial and error calculation. A second factor, which would produce errors in the opposite direction from the U-Al absorption, is the geometric effect of the non-uniform \( \text{U}_3\text{O}_8 \) particles on the diffraction characteristics. Not all the particles will contribute to the diffraction since some will be effectively shielded by the overlying metal matrix. For the same reason, not all of even the particles reaching the specimen surface will contribute. Further, the smaller particles would be characterized by diffraction behavior different from that of the larger particles and the nature of the
diffraction would be influenced by the sphericity of the individual particles. This factor presents exceedingly complex questions as to calculation of a correction factor.

Since complete correction of the x-ray data was indisputably beyond the scope of the program, the decision was made to evaluate only two relatively simple factors to indicate the complexity of the problem and to show the compensating nature of the corrections which can be predicted.

A. Absorption Correction

As the UO₂ in the outer reaction layer is further reduced, the resulting Al₂O₃ forms an x-ray absorbing zone which tends to shield the underlying UO₂. As an approximate correction for this shielding, the equation

\[ I = I_0 e^{-\mu x} \]  

may be used in which

- \( I = \) diffracted intensity with Al₂O₃ absorber present
- \( I_0 = \) diffracted intensity in absence of Al₂O₃ layer
- \( \mu = \) absorption coefficient
- \( x = \) mean distance travelled by x-ray beam in absorber.

For an average diffraction angle \( \theta \), the distance travelled in the absorber is related to the absorber thickness by

\[ x = \frac{2t}{\sin \theta} \]  

The absorber thickness is determined by the conversion of U₃O₈ to Al₂O₃ and U-Al solution. Since the absorption is determined by the mass of Al₂O₃ traversed, essentially the same result will be obtained by considering the outer layer to be fully compacted with a density of 3.9 gm/cc or to be
porous, conforming to the original $U_3O_8$ particle size, and of 32 per cent lower density. Taking the alumina layer as being fully dense, for convenience, shows that

$$\frac{t_A}{r_0} = [0.672(1-C) + C]^{1/3} - C^{1/3} \quad B-3)$$

where

\[ r_0 = \text{original } U_3O_8 \text{ particle radius} \]

\[ C = \text{fraction of } U_3O_8 \text{ not converted to U-Al solution} \]

Combination of Equation B-1, and B-2 shows that

$$I = I_0 \exp \left[ - \frac{2\mu r_0}{\sin \theta} \left( \frac{t_A}{r_0} \right) \right] \quad B-4)$$

Comparing the ratio of the absorption corrected intensities at two different degrees of reaction with the ratio of the uncorrected intensities shows that

$$\frac{(I_0')_2}{(I_0')_1} = \frac{I_2}{I_1} \exp \left[ - \frac{2\mu r_0}{\sin \theta} \left[ \left( \frac{t_A}{r_0} \right)_1 - \left( \frac{t_A}{r_0} \right)_2 \right] \right] \quad B-5)$$

in which the values of $\frac{t_A}{r_0}$ are related to the residual $U_3O_8$ by Equation B-3.

Defining the absorption correction factor as

$$\psi_a = \frac{(I_0')_2 / (I_0')_1}{I_2 / I_1},$$
\[ \psi_a = \exp \left[ \frac{2\mu r_0}{\sin \theta} \left( \frac{t_A}{r_0} \right)_1 - \left( \frac{t_A}{r_0} \right)_2 \right] \]
B. Non-homogeneity Correction Factor

Since the U, O, and Al atoms are not homogeneously dispersed, the $\text{UO}_2$ concentration will not be linearly proportional to the diffraction peak area. The $\text{UO}_2$ particles will essentially represent "black holes" since no x-ray photon which impinges on them can be transmitted through to the aluminum below, as a result of the high $\text{UO}_2$ mass absorption. The x-ray intensity will thus be proportional to the projected $\text{UO}_2$ target area. The extent of this correction can be shown to be greatest when the projected area is set by the major $\text{UO}_2$ particle diameter. Under these circumstances, the $\text{UO}_2$ volume fraction can be calculated by setting

$$\frac{(I_o)_2}{(I_o)_1} = \frac{(A_p)_2}{(A_p)_1}$$  \hspace{1cm} B-7)

where the projected area, $A_p$, is

$$A_p = \pi r^2.$$  \hspace{1cm} B-8)

Since

$$c = \left(\frac{r}{r_0}\right)^3,$$

$$A_p = \pi c^{2/3} r_0^2$$  \hspace{1cm} B-9)

and

$$\frac{(I_o)_2}{(I_o)_1} = \frac{c_2^{2/3}}{c_1^{2/3}}$$  \hspace{1cm} B-10)
so that

\[
\frac{C_2}{C_1} = \left[ \frac{I_0}{I_0'} \right]^{3/2}. \tag{B-11}
\]

If the non-homogeneity correction factor is defined as

\[
\psi_H = \frac{C_2/C_1}{\frac{I_0}{I_0'}^{2}} \tag{B-12}
\]

then

\[
\psi_H = \frac{(I_0)^2}{(I_0')^2}^{1/2} \tag{B-13}
\]
C. Solution Procedure

The correction factors for absorption and non-homogeneity are interdependent. While Equations B-5 and B-11 could be combined to yield an equation with the concentration ratio as the only unknown, trial and error solution would be required. An equally convenient solution procedure is based on the trial loop:

1. Calculate $C_2$ from Equation B-12 using the known values for $C_1$, $I_2$, and $I_1$, neglecting the absorption correction.

2. Calculate $(I_0)_2/(I_0)_1$, from Equation B-5 using the value of $C_2$ calculated in Step 1.

3. Calculate $C_2$ from Equation B-11 using the value of $(I_0)_2/(I_0)_1$, calculated in Step 2.

4. Iterate until the solution converges.

This solution procedure is aided by Figures 6 and 7. Figure 6 shows the thickness ratio $t_A/t_o$ as a function of residual $U_3O_8$. In Step 2, the ratio for point 2 is determined from the estimate of $C_2$ calculated in Step 1. The ratio for point 1 is determined from the known value for $C_1$. The difference in these two thickness ratios is determined and the absorption correction factor, $\Psi_A$, is found from Figure 7. This factor is used to calculate $(I_0)_2/(I_0)_1$, completing Step 2.

It is apparent that the corrections for x-ray absorption in the $Al_2O_3$ and for non-homogeneity are compensating and that both approach unity as

\[Since the solution depends on the initial $U_3O_8$ particle size, which is not known, a representative value must be assumed. Calculations were made for diameter of 30 and 40 microns.\]
Figure 6. $\text{Al}_2\text{O}_3$ Surface Layer Thickness as a Function of Unreacted $\text{U}_3\text{O}_8$. 
Figure 7. Absorption Correction Factor as a Function of Al₂O₃ Thickness Ratio Difference.
the difference in conversion at points 1 and 2 becomes small. For this reason and since the trial and error solution is quite tedious, only the extrapolated equilibration reaction data were corrected. The other data used in drawing Figure 3 were not corrected. Since the absorption correction generally overcomes the non-homogeneity correction, the points in Figure 3 are too high. Failure to correct the data for Figure 3 should thus yield reaction rate estimates which are too high.

The equilibration reaction extrapolations were made using the above procedure with the results of the chemical analysis at termination of the run and the x-ray diffraction area read from the curve through the data points at the time the run was stopped. This value was used, rather than the last diffraction measurement, to compensate for statistics and inaccuracies in the area measurement which would be more pronounced at the lower intensities obtained at the end of the run.
APPENDIX C

ERROR ANALYSIS

In all of the runs involving chemical analysis, there are two obvious sources of error, the uncertainty in the residue content of the unfired dispersion and the lack of accuracy of the UO$_2$ analysis.

A. Residue Error

Since the fuel meat thickness was only 20 mils in the 100 mil plate and since the thickness tolerance of the plate was 10 per cent, some variation in the residue content was anticipated. In order to determine this variation, twenty specimens were cut at random from the plate and analyzed by methanol-iodine dissolution. The results of this study are given in Table XIII.

The variation in initial residue content alone, neglecting any errors in the specimen analysis, can produce an error in the indicated extent of U$_3$O$_8$ reduction to U-Al solution, as shown from Equation A-1, of

$$E_r(U-Al \text{ soln}) = \pm \frac{0.002338}{0.08709} \times 147.7 \pm 4.15\%$$

at the 95 per cent level of confidence.

In the indicated extent of reduction to UO$_2$, the systematic error due to the non-uniform residue content, as shown from Equation A-2, is

$$E_r(UO_2) = \pm \frac{0.002448}{0.08709} \times \text{Indicated reduction}$$

The maximum value of this error is thus

$$E_r(UO_2)_{\text{max}} = \pm \frac{0.002448}{0.08709} \times 100 \pm 2.81\%$$
TABLE XIII

DETERMINATION OF RESIDUE CONTENT

<table>
<thead>
<tr>
<th>Blank No.</th>
<th>Residue (gm/gm of specimen)</th>
<th>Blank No.</th>
<th>Residue (gm/gm of specimen)</th>
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<td>0.08730</td>
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<tr>
<td>10</td>
<td>0.08780</td>
<td>20</td>
<td>0.08810</td>
</tr>
</tbody>
</table>

\[ \overline{x} = 0.8709 \]
\[ s^2 = 0.000027359736 \]
\[ s = 0.00523 \]

Range of average at 95% level of confidence = \( \pm 0.002448 \)

Range of average at 99% level of confidence = \( \pm 0.003346 \)
B. Weighing Error

Since the percentage of $\text{U}_3\text{O}_8$ reduced to $\text{UO}_2$ is given as

$$U_0 = 2630 \frac{W}{R}$$

by Equation A-2, the weight change corresponding to a given conversion is

$$W = \frac{R}{2.631} U_0 \text{ mg.} = 0.0331 U_0 \text{ mg.}$$

For complete conversion to $\text{UO}_2$, the weight change is only 3.31 mg. per gram of sample. The accuracy of weighing was only $\pm 1.5$ mg. with the old balance. The error in the $\text{U}_3\text{O}_8$ converted to U-Al solution due to the $\text{UO}_2$ analysis is then

$$E_w(\text{U-Al soln}) = \pm \frac{167 (0.0015)}{0.08709} = \pm 2.88\%$$

The maximum error in the $\text{U}_3\text{O}_8$ converted to $\text{UO}_2$, due to weighing inaccuracy alone is

$$E_w(\text{UO}_2) = \pm \frac{0.0015}{0.00331} (100) = 45.3\%$$

If the $\text{UO}_2$ analysis is considered completely erroneous, the maximum error in the calculation of $\text{U}_3\text{O}_8$ reduced to U-Al solution is

$$E_w(\text{U-Al soln.}) = \pm \frac{167 (0.00331)}{0.08709} = \pm 6.35\%$$

With the new balance, the weighing accuracy was sufficient not to produce errors of this type.
C. Errors in Conversion Results

The errors discussed in parts A and B above produce predictable errors in the values for $\text{U}_3\text{O}_8$ conversion as summarized in Table XIV.

**TABLE XIV**
PREDICTABLE ERRORS IN CHEMICAL ANALYSIS

<table>
<thead>
<tr>
<th></th>
<th>New Balance ($% \text{U}_3\text{O}_8$)</th>
<th>Old Balance ($% \text{U}_3\text{O}_8$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{U}_3\text{O}_8$ Conversion to $\text{U}-\text{Al}$ Solution</td>
<td>$\pm 4.15$</td>
<td>$\pm 10.5$</td>
</tr>
<tr>
<td>$\text{U}_3\text{O}_8$ Conversion to $\text{UO}_2$</td>
<td>$\pm 2.81$</td>
<td>$\pm 100$</td>
</tr>
</tbody>
</table>

In addition to the predictable errors summarized above, other random errors due to humidity, operator differences, etc., would be anticipated. These errors cannot be estimated without further work.

In view of the conservative approach applied to development of the calculated values of the energy release in Table XI, the predictable errors of Table XIII were not independently included.
APPENDIX D

STATISTICAL ANALYSIS OF DATA IN TABLE III A

Standard statistical analysis was applied to test the means. The results of this analysis are given in Table XV.
### TABLE XV

**STATISTICAL ANALYSIS OF DATA FROM TABLE III A**

#### UO₂ Analysis

<table>
<thead>
<tr>
<th></th>
<th>1800°F</th>
<th>1900°F</th>
<th>1950°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimate</td>
<td>2.4651</td>
<td>1175²</td>
<td>+ 1/5</td>
</tr>
<tr>
<td>Variance ($s^2$)</td>
<td>14.2333</td>
<td>97.8580</td>
<td>181.6030</td>
</tr>
<tr>
<td>Standard Deviation ($s$)</td>
<td>3.77</td>
<td>9.89</td>
<td>13.48</td>
</tr>
</tbody>
</table>

**Sum of squares**

<table>
<thead>
<tr>
<th></th>
<th>Degree of Freedom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Within Groups</td>
<td>110.7696</td>
</tr>
<tr>
<td>Between Groups</td>
<td>6.6500</td>
</tr>
</tbody>
</table>

\[ F = \frac{6.6500}{110.7696} = 0.06004 \]

\[ F_{0.05, 2/13} = 3.8056 \text{ (Not significant)} \]

#### U-Al Soln. Analysis

<table>
<thead>
<tr>
<th></th>
<th>1800°F</th>
<th>1900°F</th>
<th>1950°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimate</td>
<td>1800°F</td>
<td>1900°F</td>
<td>1950°F</td>
</tr>
<tr>
<td>Variance ($s^2$)</td>
<td>22.8200</td>
<td>2.9907</td>
<td>9.1630</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>4.78</td>
<td>1.73</td>
<td>3.03</td>
</tr>
</tbody>
</table>

\[ t_{1900-1950} = \frac{12.75 - 10.07}{2.4651 \sqrt{1/5 + 1/5}} = 1.8832 \]

\[ t_{0.05, 10} = 2.2281 \text{ (Not significant)} \]

\[ t_{1800-1900} = \frac{10.07 - 3.77}{3.1529 \sqrt{1/3 + 1/5}} = 3.3412 \]

\[ t_{0.025, 8} = 2.7515 \text{ (Significant)} \]
APPENDIX E

CALCULATION OF ENERGY RELEASE

To illustrate the procedure, the estimated equilibration energy release at 1850°F is calculated.

Reduction to UO$_2$:

No value at 1850°F appears in Table VII. According to Rule 3 (page 46), the value at 1900°F was used.

Reduction to UO$_2$ = 66%

Reduction to U-Al solution:

No value appears at 1850°F in Table VI. According to Rule 3, the value at 1900°F was used.

Reduction to U-Al solution = 31%

According to Rule 4, had the sum of this figure and that for reduction to UO$_2$ exceeded 100%, a value for the reduction to U-Al solution would have been calculated by setting:

Reduction to U-Al solution = 100 - reduction to UO$_2$.

Maximum Equilibration Energy Release:

\[
\Delta H = 0.66 (228.9) + 0.31 (445.9) = 289 \text{ kcal/kg } U_3O_8
\]

where the values of 228.9 and 445.9 were drawn from Table IX.

Minimum Equilibration Energy Release:

\[
\Delta H = 0.66 (228.9) + 0.31 (264.5) = 233 \text{ kcal/kg } U_3O_8
\]

where the values of 228.9 and 264.5 were drawn from Table IX.
APPENDIX F

REACTION IN Al-41 W/O U₃O₈ DISPERSION

After completion of this report, measurements were made of the extent of reaction in rolled Al-41 w/o U₃O₈ plates 1/. The samples were run in exactly the same manner as the 1950°F specimens listed in Table III A, page 24, of this report. The results of the study are summarized in Table XVI.

TABLE XVI

RESULTS OF TESTS ON Al-41 w/o U₃O₈ DISPERSION

<table>
<thead>
<tr>
<th></th>
<th>gm disp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residue Content of Blanks *</td>
<td>0.18961 ± 0.00550</td>
</tr>
<tr>
<td>Residue Content of Fired Specimens *</td>
<td>0.18286 ± 0.01350</td>
</tr>
<tr>
<td>Weight Gain on Oxidation *</td>
<td>0.00318 ± 0.00103</td>
</tr>
<tr>
<td>Conversion to U-Al Solution **</td>
<td>8.1 ± 15.7%</td>
</tr>
<tr>
<td>Conversion to UO₂ **</td>
<td>44 ± 15.6%</td>
</tr>
</tbody>
</table>

* Limits shown are for the 95 per cent level of confidence in the average, 10 samples.

** Limits shown were obtained by partial differentiation of Equations A-1 and A-2, page 55, and calculation of the values of the resultant error components. Should exceed the 95 per cent level of confidence.

1/Plates courtesy of Phillips Petroleum Company, Mr. Warren K. Francis.
The results of Table XVI were compared with the corresponding results of Table III A using a t test. Neither the conversion to UO$_2$ nor to U-Al solution showed a significant difference at the 95 per cent level of confidence. On the basis of this limited test, the 34 w/o and 41 w/o dispersions cannot be said to show different extents of reaction during the heating cycle employed.
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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
U. S. Atomic Energy Commission
Oak Ridge Operations Office
Oak Ridge, Tennessee

Contract No. AT-(40-1)-2483

1 September 1964

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia
ENGINEERING EXPERIMENT STATION

of the Georgia Institute of Technology

Atlanta, Georgia

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

U. S. Atomic Energy Commission
Oak Ridge Operations Office
Oak Ridge, Tennessee

November 14, 1958 to July 1, 1964
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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-U$_3$O$_8$ 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.
 § 1.1

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.
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:
§ 1.3 Nomenclature

Considerable confusion has arisen in the literature as to proper appel- lation 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.
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*

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<th>Form</th>
<th>Bulk, Not Shaped</th>
<th>Simple Shapes</th>
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<td>Transparent, Optical Grade</td>
<td>40</td>
<td>80</td>
</tr>
<tr>
<td>Transparent, Utility Grade</td>
<td>16</td>
<td>30</td>
</tr>
<tr>
<td>Translucent</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Slip-Cast</td>
<td>0.5</td>
<td>1.5</td>
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*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


CHAPTER II
THE STRUCTURE OF FUSED SILICA

§ 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 ($\text{SiO}_2$). 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 $4.5 \times 10^{-2}$ and $7.7$ microns per minute at 2860°F 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 \( \beta \) high temperature form of cristobalite to the \( \alpha \) 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 \( \alpha \)-\( \beta \) 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 $1.60 \pm 0.05\text{Å}$ and the Si-Si distance is $3.00 \pm 0.05\text{Å}$. 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 anomalous 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 Å 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 Å.

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 $\alpha$-quartz exists over a region greater than 5 Å.

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 Å 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 Å 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 50-100 Å 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.
§ 2.10 - § 2.11

**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 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

\[/\text{See § 2.8.}\]
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 ultraviolet 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.

§ 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 cission 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 cission 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.

§ 2.15 References for Chapter II


37. Ibid. at p. 56.
38. Ibid. at p. 61.
39. Ibid. at p. 86.
§ 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
§ 3.1 - § 3.2

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

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1/See § 3.8.
2/See § 3.9.
TABLE II
SURFACE CONTAMINANTS IN SLIP-CAST SILICA

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

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/.

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.
§ 3.6 - § 3.7

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

<table>
<thead>
<tr>
<th></th>
<th>Wet Milled Slip</th>
<th>Dry Milled Slip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Approximate Solids Content (w/o)</td>
<td>83</td>
<td>69</td>
</tr>
<tr>
<td>Viscosity (cp)</td>
<td>130</td>
<td>80-120</td>
</tr>
<tr>
<td>pH</td>
<td>5.2</td>
<td>1-2</td>
</tr>
</tbody>
</table>

1 Glasrock Products, Inc.
2 Schulle (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

<table>
<thead>
<tr>
<th>Element</th>
<th>Content (Approximate) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.004</td>
</tr>
<tr>
<td>Al</td>
<td>0.008</td>
</tr>
<tr>
<td>Fe</td>
<td>0.008</td>
</tr>
<tr>
<td>Ca</td>
<td>0.001</td>
</tr>
<tr>
<td>Mg</td>
<td>0.001</td>
</tr>
<tr>
<td>Ti</td>
<td>0.001</td>
</tr>
</tbody>
</table>

§ 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.

\[(W + W_c)^2 = K (\theta + \theta_c)\]  \hspace{1cm} (1)

where \( W \) = cast wall thickness
\( W_c \) = cast wall thickness having same resistance to filtrate flow as the plaster
\( K \) = pressure dependent constant
\( \theta \) = casting time
\( \theta_c \) = casting time to form the fictitious wall \( W_c \)

The values of \( W_c \), \( K \) and \( \theta_c \) 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 \( \theta_c \) 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.
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 $\theta_c$ is approximately inversely proportional to the pressure. Since $\theta_c$ is small, Equation 1 may be rewritten

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

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)
$\theta$ = time (min)

The negative value of $\theta_c$ 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

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

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.
§ 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.
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 M²/gm |
| Cast, Unfired: | 5.24 M²/gm |

<table>
<thead>
<tr>
<th>Firing Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000° F</td>
</tr>
<tr>
<td>(M²/gm)</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td>16</td>
</tr>
</tbody>
</table>

* 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


4. Ibid. at p. 498.


15. Ibid. at p. 51.

16. Ibid. at p. 81.


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


28. Ibid. at p. 13.

29. Ibid. at p. 18.


31. Ibid. at p. 27.

32. Ibid. at p. 55.


34. Ibid. at p. 31.

35. Ibid. at p. 33.
CHAPTER IV
PHYSICAL PROPERTIES

§ 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.
§ 4.2 - § 4.4

TABLE VII

ROOM TEMPERATURE STRENGTH OF BULK FUSED SILICA

<table>
<thead>
<tr>
<th></th>
<th>Tensile (psi)</th>
<th>Compressive (psi)</th>
<th>Transverse (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparent</td>
<td>10,400</td>
<td>93,000</td>
<td>16,000</td>
</tr>
<tr>
<td>Translucent</td>
<td>3,200</td>
<td>44,400</td>
<td>6,400</td>
</tr>
<tr>
<td>Slip-Cast (Air Firing)</td>
<td>4,300</td>
<td>23,000</td>
<td>4,700</td>
</tr>
</tbody>
</table>

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 (30) 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 deter-
mined by Westbrook (74). As shown by Mackenzie, the hardness in the range of
900°F 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 x 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 measure-
ments 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

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

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

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°F 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°F 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). 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).

\[1/\text{See § 2.13.}\]
TABLE VIII
DENSITY AND THERMAL EXPANSION COEFFICIENT
OF TRANSPARENT FUSED SILICA WITH DIFFERENT WATER CONTENT

<table>
<thead>
<tr>
<th>Type</th>
<th>Water Content (w/o - OH)</th>
<th>Density (gm/cc)</th>
<th>Average Thermal Expansion Coefficient (32-212°F) (°F⁻¹ x 10⁷)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrically Fused</td>
<td>0.0003</td>
<td>2.203</td>
<td>2.67</td>
</tr>
<tr>
<td>Flame Fused</td>
<td>0.040</td>
<td>2.201</td>
<td>----</td>
</tr>
<tr>
<td>Synthetic</td>
<td>0.125</td>
<td>2.197</td>
<td>2.89</td>
</tr>
</tbody>
</table>

*Equilibrium Temperature = 1900°F.

The preceding 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
The elastic compressibility of fused silica is quite reproducible at low pressures. At one atmosphere, this compressibility has been determined to be $9.9 \times 10^{-7}$ 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). 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.

§ 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:

\[
\begin{align*}
\text{SiO}_2(s) & \rightarrow \text{SiO}_2(g) \\
\text{SiO}_2(s) & \rightarrow \text{SiO}(g) + \frac{1}{2} \text{O}_2(g) \\
2\text{SiO}(g) & \rightarrow \text{Si}_2\text{O}_2(g) \\
\text{O}_2(g) & \rightarrow 2\text{O}(g)
\end{align*}
\]

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

\[\text{permeation of hydrogen}\]

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.

§ 4.14 References for Chapter IV


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


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


§ 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.

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...
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).

§ 5.6 References for Chapter V

8. Ibid, p. 897
Figure 40. Heat Capacity of Fused Silica.
Figure 41. Enthalpy of Fused Silica.
Figure 42. Heat and Free Energy of Formation of Fused Silica.


§ 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.
§ 6.1 - § 6.2

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 cission 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 Al₂O₃ (12) or B₂O₃ (11) suppress devitrification, this has been refuted (5,14). B₂O₃ 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 Al₂O₃ increases the devitrification rate (5).

1/See § 2.13.
In general, the sequence of decreasing effect in promoting devitrification is (17):

\[
\begin{align*}
\text{K} & \quad \text{Na} \\
\text{Li} & \quad \text{Ba} \\
\text{Pb} & \quad \text{Fe}^{+2} \\
\text{Zn} & \quad \text{Mg} \\
\text{Fe}^{+3} & \quad \text{Al} \\
\text{Ti} &
\end{align*}
\]

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.

If these factors are such as to render divitrification 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

\[1/\text{See § 7.17.}\]
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).

§ 6.12 References for Chapter VI


NOTE: The following references are to reports issued under this contract. See Appendix B for complete listing.
§ 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 results in changes of its x-ray diffraction pattern consisting of slightly increased diffraction peak intensity (14). Further irradiation to $7 \times 10^{19}$ 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 $1 \times 10^{20}$ nvt (28), but by a dose of $2 \times 10^{20}$ 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 $1.3 \times 10^{19}$ nvt (15).

Quartz, cristobalite, tridymite, and fused silica are all transformed into an identical material by irradiation to approximately $2 \times 10^{20}$ 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).

\[ 1/nvt = \text{Neutrons/cm}^2. \]
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 $4 \times 10^{20} \text{nvt}$ 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 $300^\circ \text{K}$ neutrons (C neutrons) (3). The measured cross section is $8.0 \pm 1.0$ 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>
<thead>
<tr>
<th>Absorption (Additive)</th>
<th>0.161 Barns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macroscopic Absorption (Additive)</td>
<td>0.0035 cm$^{-1}$</td>
</tr>
<tr>
<td>Scattering (Additive)</td>
<td>10.1 Barns</td>
</tr>
<tr>
<td>Total (Additive)</td>
<td>10.2 Barns</td>
</tr>
<tr>
<td>Total (Measured, Ref. 3)</td>
<td>8.0 Barns</td>
</tr>
</tbody>
</table>

§ 7.6 Effects on Strength
Thompson found that irradiation at $212^\circ \text{F}$ to $2.4 \times 10^{18} \text{nvt}$ and at $-321^\circ \text{F}$ to $1.6 \times 10^{18} \text{nvt}$ left the strength of transparent fused silica unchanged within $\pm 10$ per cent (26).

Fleming irradiated slip-cast fused silica to calculated dose levels of from approximately $2 \times 10^{20}$ to $6 \times 10^{20} \text{nvt}$ (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 $3 \times 10^7$ (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 $5 \times 10^{19}$ 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 $8 \times 10^{19}$ to $4 \times 10^{20}$ 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 $\text{1/}$ by fast neutrons. This is complete by about $3 \times 10^{20}$ 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 $3 \times 10^{19}$ 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 $9 \times 10^7$ r. Upon further irradiation to $1.8 \times 10^8$ r, the density

\[ \text{1/See § 2.9.} \]
§ 7.10

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

§ 7.11 Thermal Expansion

Simon measured the thermal expansion coefficient of fused silica between room temperature and $400^\circ F$ after irradiation to $1.4 \times 10^{20}$ nvt (24). The value determined was $3 \times 10^{-7} \text{°}^{-1}$ 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 $-442^\circ F$ (5). The thermal conductivity increased linearly with dose, becoming doubled at the highest dose used, $6 \times 10^{19}$ nvt (19).

Bopp, et al, measured the room temperature thermal conductivity of fused silica irradiated to doses of $3 \times 10^{19}$ to $1.6 \times 10^{20}$ 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 $3 \times 10^{20}$ nvt. Samples which initially contained from 21 to 88 per cent cristobalite retained from 3 to 8 per cent cristobalite after a dose of $2 \times 10^{20}$ to $3 \times 10^{20}$ 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 $\gamma$ radiation and $10^{16}$ nvt (6). They predicted that the visual properties would not be seriously altered up to $1.4 \times 10^{17}$ 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.

§ 7.18 References for Chapter VII


19. Oak Ridge National Laboratory, Solid State Division Annual Progress Report for Period Ending 31 August 57 ORNL - 2413 (ref.).
§ 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).
Cadmium: 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).

§ 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).
§ 8.21 References for Chapter VIII


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 preceding 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 $2.5 \times 10^{10}$ cps (12). The room temperature loss tangent varies somewhat with frequency, ranging from about $8 \times 10^{-4}$ 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.

§ 9.5 References for Chapter IX

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 preceding 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/ft\(^3\) was found to have a volume resistivity of approximately \(10^{-16}\) ohm-cm. at room temperature and \(10^6\) ohm-cm. at 1830° F. Glassy foam with densities ranging from 17.4 to 46.4 lb/ft\(^3\) 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 \(10^{10}\) 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

<table>
<thead>
<tr>
<th></th>
<th>Foamsil 1/</th>
<th>No. 25 2/</th>
<th>No. 50 2/</th>
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<td><strong>Density (lb/ft(^3))</strong></td>
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<td>47</td>
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<td><strong>Modulus of Rupture (psi)</strong></td>
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<td>120</td>
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<tr>
<td><strong>Compressive Strength (psi)</strong></td>
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<td></td>
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<tr>
<td>Room Temperature</td>
<td>130-210</td>
<td>400</td>
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<tr>
<td>2000° F</td>
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<tr>
<td>(Btu/hr ft °F)</td>
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<tr>
<td>1000° F</td>
<td>----</td>
<td>---</td>
<td>0.10</td>
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<tr>
<td>1500° F</td>
<td>----</td>
<td>---</td>
<td>0.12</td>
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<tr>
<td>2000° F</td>
<td>----</td>
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<td>0.22</td>
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</tbody>
</table>

1/Pittsburgh Corning Corporation (2, 3, 4).
2/Glasrock Products, Inc. (12, 13).

## § 10.4 References for Chapter X


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

CHAPTER XI
APPLICATIONS AND MANUFACTURERS

§ 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. Boxton-Deel, 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. Dynasile Corporation
Box D
Berlin, New Jersey
(High purity fused silica)

8. Englehard Industries, Inc.
Amerisil 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)

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. 0. 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)
§ 11.8 References for Chapter XI

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:


APPENDIX C

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Idaho Falls, Idaho
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### CONVERSION FACTORS

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<tr>
<td>gallons</td>
<td>liters</td>
<td>3.785</td>
</tr>
<tr>
<td>inches</td>
<td>cm.</td>
<td>2.540</td>
</tr>
<tr>
<td>in.²</td>
<td>cm.²</td>
<td>6.452</td>
</tr>
<tr>
<td>lb.</td>
<td>kg.</td>
<td>0.4536</td>
</tr>
<tr>
<td>lb/ft.³</td>
<td>gm./cc.</td>
<td>0.01602</td>
</tr>
<tr>
<td>lb/in.² (psi)</td>
<td>kg./m.²</td>
<td>703.1</td>
</tr>
</tbody>
</table>