

FUSED SILICA MANUAL

BY

JULIAN D. FLEMING

AND OTHERS.

VOLUME 1

Project B-153

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

Contract No. AT-(40-1)-2483

Engineering Experiment Station  
Georgia Institute of Technology  
Atlanta, Georgia  
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# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

January 15, 1959

Research and Development Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Mr. W. J. Larkin

Subject: Monthly Letter Report No. 2, Project No. B-153  
Covering the Period from 15 December 1958 to 15 January 1959  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

All the necessary counting and safety equipment for the tracer permeation studies were received. The Georgia Tech blanket by-products license was approved by the AEC. Suppliers of the required isotopes of the noble gases were contacted and quotations are being prepared.

Molds were made for casting permeation samples. The first specimens cast were cup shaped with 2-5/8-inch outside diameters and wall thicknesses of about 1/4 inch. Disks were made from the cup shapes by cutting off the walls. These samples appear satisfactory for the permeation studies and will be tested when the necessary isotopes are obtained.

Two experimental silica slips were obtained for preliminary fabrication studies of tensile test specimens, transverse specimens, and permeation disks. The slips were designated No. 1 and No. 2 for convenience. The only essential difference in the two slips was the particle size. The particle size of No. 1 was 10 per cent less than 1.1 microns and 90 per cent less than 34 microns.<sup>†</sup> The particle size of No. 2 was 10 per cent less than 1.3 microns<sup>†</sup> and 90 per cent less than 40 microns.

Stoddard tensile test specimens, shown in Figure 1, were cast in plaster molds using both Slip No. 1 and No. 2. These specimens were dried at about 160° C and fired in a gas kiln at about 2000° F for 2 hours. These specimens were tested at 0.125 inches per minute on a Dillon Model L tester. The average tensile strength of the No. 1 samples was 1400 psi. The average tensile strength of the No. 2 samples was 668 psi.

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<sup>†</sup> 10 per cent particle size points are estimated.



Some difficulty was experienced in obtaining tensile strengths because of the samples breaking at the intersection of the straight section with the conical holding end. A new model, designated B, was designed to make this transition more gradual. A typical B tensile test specimen and mold are shown in Figure 2. No B samples have yet been tested.

Transverse rupture strength specimens,  $3/8$  inch in diameter and 3 inches in length were cast in plaster molds, cured and fired as before, and tested with a Dillon Model L tester at 0.125 inches per minute. The No. 1 samples had an average transverse strength of 5490 psi. The No. 2 samples had an average transverse strength of 1150 psi.

Construction was completed and check runs were begun on the high temperature x-ray camera.

### II. Future Work

New silica slips will be obtained and tested to permit selection of a standard slip to cast samples for irradiation and devitrification studies.

Shell-casting studies will be initiated to determine the feasibility of casting simple, one-piece heat exchangers.

Samples of B tensile test specimens will be prepared and compared with the Stoddard specimens.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

✓  
J. D. Walton, Head  
Ceramic Branch

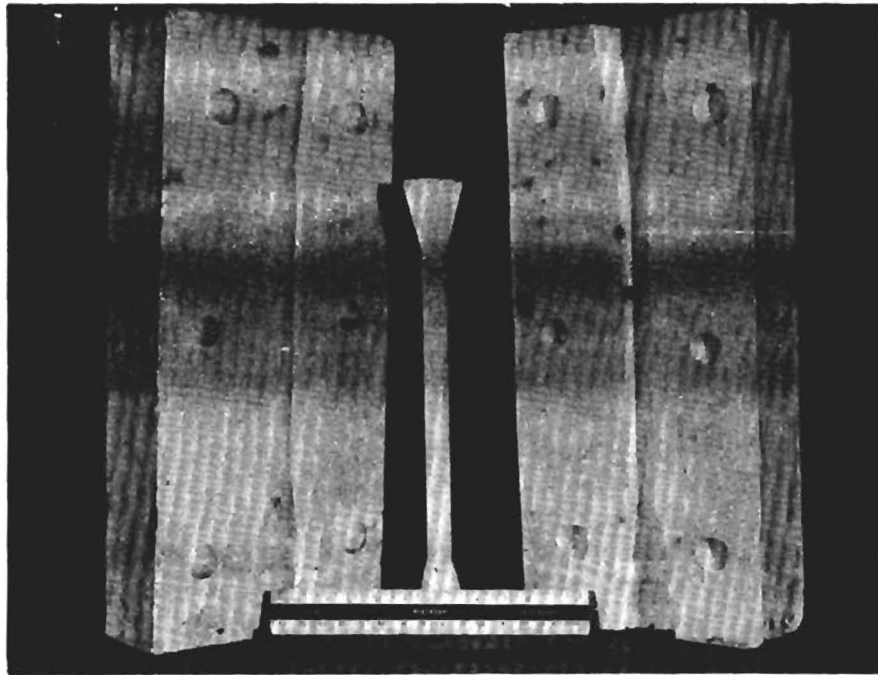


Figure 1. Stoddard Test Speciman and Mold.

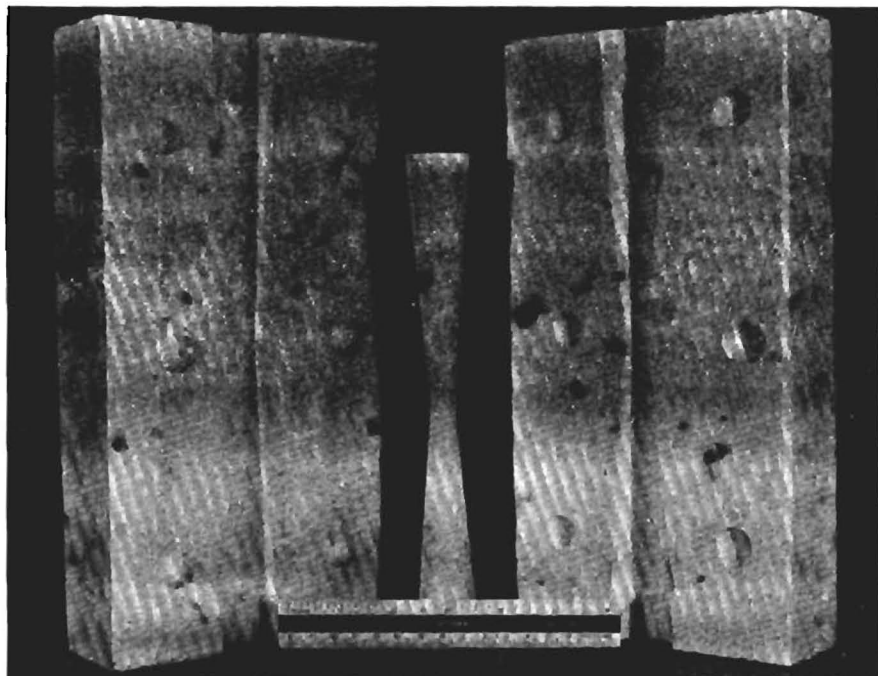


Figure 2. "B" Test Speciman and Mold.

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**ENGINEERING EXPERIMENT STATION**

**ATLANTA, GEORGIA**

B-153  
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February 16, 1959



Research and Development Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Mr. W. J. Larkin

Subject: Monthly Letter Report No. 3, Project No. B-153  
Covering the Period from 15 January to 15 February 1959  
Contract No. AT-(40-1)-2483

Gentlemen:

I. Experimental Progress

Quotations were received on A-39, Kr-85, and Xe-133. Krypton was selected for the initial permeation studies because of its low cost and immediate availability.

✓  
Experimental Slip No. 3 was obtained for strength determinations. Slip No. 3 had a particle size of 10 per cent less than 0.9 micron and 90 per cent less than 35 microns.

"B" tensile test specimens, described in Monthly Letter Report No. 2, were cast in plaster molds using Slip No. 3. Samples were cast in both vertical and horizontal molds. The samples were fired in a gas kiln at 2090° F for 2 hours. Both types were tested at 0.125 inches per minute on a Dillon Model L tester. No noticeable difference was detected in the two fabrication techniques. For 37 samples, 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. The trend, shown by Slips No. 1 and 2, for strength to be increased by a smaller particle size is qualitatively followed by Slip No. 3. Construction of the furnace for high temperature tensile testing was completed.

Fabrication studies were begun on casting single tube shell and tube heat exchangers. Because of the greater difficulty involved in casting integral exchangers, the first castings were made of the shell only. Some cracking was noticed in the shell but this is thought to be due primarily to mold sticking and should be capable of elimination.

In order to furnish a basis for predicting the cross section of the basic fused silica to be subjected to in-pile irradiation, an emission spectrograph was run on Slip No. 3. The slip contained roughly 0.1 - 0.5 per cent magnesium,

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0.5 - 3 per cent iron, 0.1 - 0.5 per cent copper, and traces of titanium, aluminum and calcium. The iron did not appear chemically bound and should be capable of being removed by acid leaching.

Samples of cristobalite were obtained from U. S. Steel and the Bureau of Standards. A sample of the amorphous silica used in the tensile tests was devitrified at 2400° F for a period of 48 hours. These three samples were compared for cristobalite content by x-ray diffraction and found to be equally crystalline. Based on this observation, x-ray cristobalite standards will be established by devitrification of the standard slip upon its selection.

## II. Future Work

A standard slip will be selected for future use throughout the remainder of the program.

Studies will be extended toward successful casting of integral single tube shell and tube heat exchangers.

The tensile test furnace will be tested and high temperature tensile strength determinations will be begun.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

U J. D. Walton, Head  
Ceramic Branch

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

March 18, 1959



Research and Development Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Mr. W. J. Larkin

Subject: Monthly Letter Report No. 4, Project No. B-153  
Covering the Period from 15 February to 15 March 1959  
Contract No. AT-(40-1)-2483

Gentlemen:

I. Experimental Progress

J✓ A 500-mc ampoule of Kr-85 was received from Oak Ridge. A re-encapsulation system was designed to produce approximately 3-mc ampoules which will be used for individual diffusion tests.

Experimental Slip No. 4 was tested thoroughly and evaluated for use as the standard slip for the remainder of the project. This slip was essentially a production batch of the previously tested Slip No. 3.

The particle size of Slip No. 4 was found to be 10 per cent less than 0.9 micron and 90 per cent less than 35 microns. Semiquantitative emission spectrographs on two random samples of Slip No. 4 showed approximately 0.12-per-cent-maximum-total metallic impurities. The slip contained approximately 0.001 per cent magnesium, 0.008 per cent iron, 0.008 per cent aluminum, 0.04 per cent copper, 0.0003 per cent silver, 0.001 per cent titanium, 0.0003 per cent nickel, and 0.001 per cent calcium. The average tensile strength of Slip No. 4 was approximately 1540 psi when fired in a gas kiln at about 2100° F for 2 hours.

The calibration curves were completed for x-ray diffraction determination of cristobalite content in the fused silica matrix. These curves will permit the resolution of cristobalite content within 0.25 per cent. Similar calibration curves were determined for the high temperature camera. The resolution obtainable in the high temperature camera is expected to be less than one per cent in ranges above 10-per-cent-cristobalite content and less than 2 per cent below 10 per cent cristobalite.

Investigations were begun to determine the influence of firing temperature and firing time on the mechanical properties of the slip-cast silica. Transverse test specimens were cast and fired for 2 hours in a gas kiln. The firing temperatures were determined only approximately by the use of pyrometric cones. Four representative transverse samples were analyzed by x-ray diffraction for cristobalite content. The results of the exploratory investigation showed that the strength to increase with firing temperature was apparently a result of higher cristobalite formation. These results are summarized in Table I.

TABLE I

EFFECT OF FIRING TEMPERATURE ON MODULUS OF RUPTURE

<u>Firing Temperature (Approx.)</u> (° F)	<u>Modulus of Rupture</u> (PSI)	<u>Cristobalite Content</u> (%)
2050	2000	0.85
2090	3140	1.2
2100	4700	1.5
2160	5175	2.4

Studies were begun to determine the effect of testing temperature on the tensile strength of the slip-cast fused silica. Because of faulty design and operation, the furnace on the tensile-testing machine burned out early in the study. Although insufficient results were obtained prior to burn-out of the furnace, to concretely establish a trend, the tensile strength appeared to increase with testing temperature. Tentative results indicated that the tensile strength may be increased by as much as 30 per cent at 2000° F.

Techniques were developed by which integral single tube shell and tube heat exchangers could be cast. The tendency of the shell to crack was eliminated by coating the plaster molds with a layer of graphite.

## II. Future Work

The influence of firing temperature and firing time on the strength of the slip-cast fused silica will be more extensively investigated.

X-ray diffraction studies will be coupled with electron microscopy and physical testing to determine the mechanics of the cristobalite formation. Attempts will be made to relate the mode of formation to the increase in strength noted with higher cristobalite content. In particular, an examination will be made of the possibility of nucleation and growth across particle boundaries, resulting in greater cross-linking of the particles.

Research and Development Division  
Oak Ridge Operations Office

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High temperature x-ray diffraction studies will be begun to establish nucleation and crystallite growth curves for the slip-cast silica.

Methods will be developed for joining the simple fused silica heat exchangers to conventional water and steam lines. Upon successful completion of this study, experiments will be initiated to establish typical heat transfer characteristics of the exchangers.

Upon completion of the re-encapsulation of the Kr-85, the permeation studies and surface-sealing studies will be begun.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramic Branch

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**GEORGIA INSTITUTE OF TECHNOLOGY**  
**ENGINEERING EXPERIMENT STATION**  
**ATLANTA, GEORGIA**

April 22, 1959

Research and Development Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Mr. W. J. Larkin

Subject: Monthly Letter Report No. 5, Project No. B-153  
Covering the Period from 15 March to 15 April 1959  
Contract No. AT-(40-1)-2483



Gentlemen:

I. Experimental Progress

✓✓ The re-encapsulation system designed to produce 3-mc ampoules was tested in a dry run using capsules containing air. Consideration of the apparatus indicated that the radioactive krypton would be trapped in a bellows through which the capsule-breaking plunger was introduced into the system. This observation resulted in a reworking of the system to completely eliminate any gas-trapping crevices.

Preliminary studies were made up to 1800° F to determine the effect of temperature on the tensile strength of slip-cast fused silica. "B" tensile test specimens, described in Monthly Letter Report No. 2, were cast in plaster molds. The bars were air dried and fired at 2100° F for two hours in a gas kiln. Six specimens were tested at each temperature using a Dillon Model L tester operating at a crosshead speed of 0.125 inches per minute. The results of the tests are summarized in Table I.

In order to prevent heating the holding fixtures, the high temperature furnace on the tensile tester was so constructed as to heat only the central 3 inches of the specimen. This resulted in portions of the sample with less than three times the cross sectional area of the central zone being cold during the test. As the testing temperature was increased, therefore, many of the samples broke outside of the hot zone because of the great increase in strength of the silica with temperature. In calculating the tensile strengths of specimens which broke outside of the hot zone, the area of the hot zone was used. These strengths consequently represented only the highest test stresses which were applied, and not the true tensile strength of the silica. Because of the high percentage of breaks outside the hot zone at temperatures of 1600° and 1800° F,



TABLE I  
EFFECT OF TESTING TEMPERATURE ON SHORT-TIME TENSILE STRENGTH

<u>Testing Temperature</u> (° F)	<u>Tensile Strength</u> (PSI)
70	1200
200	1200
400	1200
600	1300
800	1600
1000	1800
1200	2000
1400	2300
1600	> 2600
1800	> 3600

the tensile strengths at these temperatures could only be roughly approximated. At higher temperatures, essentially no hot zone breaks were obtained. Attempts were begun to increase the strength of the cold zone of the tensile test bars by resin soaking in order to decrease the tendency of the bars to break outside the hot zone.

The investigation of the influence of firing temperature and firing time on the modulus of rupture of the slip-cast fused silica was shifted to a Globar fired tube furnace to provide better temperature control. At a specified temperature, indicated on the furnace control, a temperature profile was obtained by reading a thermocouple placed at measured positions in the tube. From the profile, the firing temperature of articles in the tube could be accurately estimated.

Studies were begun of the modulus of rupture of bars fixed at temperatures of 2100°, 2200°, 2300° and 2400° F for 2, 4, 8 and 16 hours. Initial results from the 2100° and 2200° F firings indicated an initial increase in fired strength with firing time and firing temperature, perhaps due to an intergranular cristobalite formation. This initial increase was followed by a decrease in strength on longer or higher temperature firing, probably due to extensive cristobalite formation which would weaken the bars during sudden cooling from the firing temperature.

April 22, 1959

High temperature x-ray diffraction investigations were begun to determine the kinetics of cristobalite formation in the slip-cast fused silica. Difficulties were immediately encountered in accurate measurement of the temperature of the sample. A thermocouple on the back of the sample holder failed to indicate the true sample temperature because of the temperature drop across the silica. Since the devitrification process in silica seems to depend greatly on temperature, small errors in temperature measurement in the range of 2100° F could completely invalidate the devitrification test results. In order to minimize the temperature errors, calibration runs were begun using materials, such as quartz, which undergo sharp phase transformations at well-known temperatures. These calibrations were carried out by spreading a very thin layer of the test material over a fused silica sample in the sample tray. Determination of the thermocouple temperature at the point of trace change gave the calibration point.

## II. Future Work

The resin-soaked tensile test specimens will be tested at 2000° F to determine the ability of the treatment to eliminate cold zone fractures. If this treatment fails to yield satisfactory results, the specimen will be redesigned to have a larger cold zone area and smaller hot zone area.

The firing temperature and time studies will be extended and correlated with cristobalite growth.

Temperature calibrations of the high temperature x-ray camera will be completed and cristobalite growth curve determinations will be started.

The Kr-85 will be re-encapsulated in the modified handling system and permeation investigation will be started.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramic Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

May 21, 1959

Research and Development Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Mr. W. J. Larkin

Subject: Monthly Letter Report No. 6, Project No. B-153  
Covering the Period from 15 April to 15 May 1959  
Contract No. AE-(40-1)-2483

Gentlemen:

## I. Experimental Progress

✓ Attempts were made to prevent cold-zone fractures in the high temperature tensile tests by strengthening the ends of the test bars with various additives. Filling the ends of the bars with phenolic resins and with silica, deposited from hydrolyzed ethyl silicate, increased the cold-zone strength by at least 50 per cent. This increase in strength was ineffective in preventing cold-zone fractures at 2000° F. Of six bars prepared in this manner, only one broke in the hot zone at 2000° F.

An evaluation of systems which would eliminate cold-zone breaks indicated that the most practical would be one which would uniformly heat the entire silica test specimen. In trying to locate alloys with suitable high temperature strength to be used as heated holding fixtures, a reference was found to holders fabricated for ORNL by the Inco Investment Castings Company. These holders were found to be of ideal size and design for use with fused silica samples and to have sufficient high temperature strength for use at 2000° F. These holders were ordered and design was begun of the new tensile test specimens required.

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 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. Construction was begun on a steam and water supply system for testing the cast heat exchangers.

The Kr-85 was re-encapsulated in the modified handling system in approximately 5-mc ampoules. No difficulty was encountered in using the modified system. Since water displacement was used, no contamination of the system occurred.

Check runs were begun to evaluate the performance of the permeation system described in Monthly Letter Report No. 1. Permeation discs 0.25-inch-thick were used for the check runs. The discs were not sealed in any way and had porosities of approximately 10 per cent. Mathematical interpretation of the results of the check runs was begun. This treatment will be used to establish the permeation rate for unsealed silica which will be the basis for comparison of the sealing techniques to be investigated.

Firing time and temperature studies were extended to temperatures of 2240° F. In order to investigate the influence of temperature and time on the degree of particle bonding, surface area determinations were made using the standard nitrogen-adsorption technique. The surface area of the dried, unfired slip was 5.39 m<sup>2</sup>/gm. The surface area of the cast and fired samples was found to decrease detectably with firing time. Porosity determinations were begun to establish the mechanism of this surface area decrease. If the porosity, as determined by water absorption, decreases, the surface area decrease would be attributed to simple sealing of the pores. Failure of the porosity to decrease at the same rate as surface area would indicate a point-bonding mechanism.

In order to obtain an indication of the influence of size on the fired strengths of the transverse specimens, both 3/8- and 3/4-inch-diameter bars were included in the firing studies. The agreement between the strengths of the two sizes was quite good.

X-ray determinations were made of the cristobalite content of the transverse bars. In the region below 10 per cent cristobalite, these determinations are accurate to only an absolute error of 0.25 per cent. In view of this error, the fact that no correlation of cristobalite content with strength was obtained was not too surprising.

Table I lists the surface areas, strengths of 3/8- and 3/4-inch bars, and cristobalite content for the three firings for which complete data have been obtained.

Platinum-shadowed carbon replicas were made of the fired test bars for examination by electron microscopy. No conclusions could be drawn from the first samples as to the bonding made.

The high temperature x-ray camera was applied to the investigation of the devitrification rate of the fused silica slip. First results indicated a strong dependence of the devitrification rate on surface area. A necessity was indicated for modification of the camera to permit testing of fired bodies as well as powders at elevated temperatures. Tentative plans for the necessary modification were drawn up.

TABLE I  
PROPERTIES OF SLIP-CAST FUSED SILICA FIRED AT 2060° F

Firing Time (Hr)	Modulus of Rupture		Surface Area (M <sup>2</sup> /Gm)	Cristobalite Content (%)
	3/8-Inch Bars (Psi)	3/4-Inch Bars (Psi)		
2	1300	1460	2.74	1.5
4	3100	1430	2.48	1.25
8	4000	4130	1.70	1.7

A prototype of the irradiation capsules to be used in the WTR was fabricated from 6061 aluminum. The prototype was forwarded to the WTR staff for evaluation.

## II. Future Work

Tensile test specimens will be designed and fabricated for use with the Inco Company holding fixtures. Upon receipt of these fixtures and satisfactory design of the new specimens, a new furnace will be designed and constructed to provide the desired testing temperatures.

Permeation studies will be continued and sealing techniques will be investigated.

Investigations will be extended to determine the influence of firing conditions on the surface area, porosity, cristobalite content, and strength of the cast fused-silica.

Studies will be initiated to evaluate the application of selected area electron diffraction to the investigation of intergranular and intragranular cristobalite growth.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramic Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

June 17, 1959



Research and Development Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Mr. W. J. Larkin

Subject: Monthly Letter Report No. 7, Project No. B-153  
Covering the Period from 15 May to 15 June 1959  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

✓ The ORNL tensile specimen holders for high temperature testing were received from the Inco Investment Castings Company. Split aluminum master molds were machined to fit the 3/4-10 threads of the ORNL holders. From these positive aluminum masters, negative plaster molds were prepared. The cylindrical fused silica samples cast from these molds were similar to ASTM samples, threaded on both ends and with center sections reduced to either one-half or three-eighths of an inch. Some difficulty was encountered in producing bubble-free threads, but this trouble was largely eliminated by coating the aluminum masters with a detergent solution prior to casting. Firing studies were begun to determine the conditions which would produce minimum distortion in the fired samples.

The permeation studies were continued using unsealed silica discs and discs whose porosity was decreased by soaking in hydrolyzed ethyl silicate. Some leakage of Kr-85 from the system was noted. This leakage was effectively eliminated by the use of thick interface gaskets which were fabricated from overplasticized polyvinyl chloride. When coated with silicone vacuum grease, the gaskets formed a leak-free seal to the silica.

Mathematical treatments which have been investigated have failed as yet to correlate the results of the permeation studies. Qualitatively, however, soaking the permeation disc once in ethyl silicate and firing it cut the permeation rate in half. Quantitative comparisons were begun to determine the effect of porosity on the permeation rates. These comparisons will be pointed toward the development of a successful mathematical treatment.

Investigations to determine the influence of firing conditions on the strength, cristobalite content, surface area and porosity of the slip-cast fused silica were continued to 2300° F. Reduction and analysis of the data from these studies and construction of graphs to show the trends noted were begun for inclusion in Monthly Letter Report No. 8.

Studies were begun to establish the influence of cristobalite content on the thermal expansion characteristics of the slip-cast fused silica. Preliminary results of the dilatometric study indicated that the  $\alpha$ - $\beta$  cristobalite inversion would be detectable at about 10 per cent cristobalite.

Construction was begun of a platinum-wound cell furnace for use in the high temperature x-ray camera. This furnace should provide better temperature control and will permit the use of cast and fired silica as well as silica powder in the rate determinations.

The prototype of the containment capsule to be used in the irradiation of the slip-cast silica was approved by the WTR staff. Six containment capsules were fabricated and production of samples for encapsulation was begun.

## II. Future Work

Tensile strengths of the cast silica will be determined at elevated temperatures using the new threaded samples and the ORNL holders.

An intensive study will be made to yield a mathematical treatment capable of correlating the results of the permeation study.

Dilatometric studies will be continued to determine quantitatively the influence of cristobalite on the thermal expansion characteristics of the slip-cast silica.

Upon completion of the x-ray furnace, the cristobalite growth rate studies will resume.

Respectfully submitted,

J. D. Fleming *FB*  
Senior Investigator

Approved:

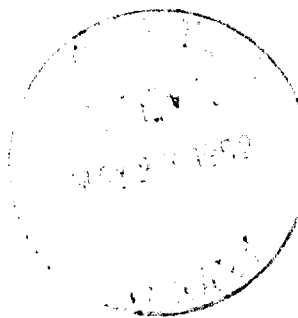
*for* J. D. Walton, Head  
Ceramic Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

July 21, 1959



Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 8, Project No. B-153  
Covering the Period from 15 June to 15 July 1959  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

DJ✓  
A tubular, resistance-heated furnace was constructed for heating the tensile test specimens to temperatures in the range of 2100° F. Several of the threaded tensile test specimens were broken at 1800° to 2000° F to determine the ability of the system to yield valid data at elevated testing temperatures. Some difficulty was encountered as a result of the sharp 75 per cent threads acting as stress concentrators and causing premature breaks. Attempts were begun to overcome this effect by rounding the threads and decreasing them to 50 per cent depth.

The preliminary test data obtained with the new specimens were combined with the data previously obtained with the older specimens. The data on the older specimens were essentially unchanged by inclusion of the recent data. Figure 1 shows the variation in tensile strength of slip-cast fused silica with temperature in the temperature range over which statistically reliable data have been obtained.

The studies to determine the influence of firing temperature and firing time on the strength of slip-cast fused silica were completed. The results of these studies are shown in Figures 2 and 3. The shapes of the curves are typical of processes in which strengthening or hardening results from precipitation of a second phase. This observation is qualitatively consistent with the postulation of particle bonding by cross-particle cristobalite growth.

Mathematical treatment of the data from the permeation experiments has successfully yielded reproducible permeation coefficients. Curves were plotted



of the hot-side and cold-side activities as a function of time. From these curves, the activity difference, or driving potential, was calculated. Graphical differentiation of the cold-side activity curve was used to calculate the differential activity change, or active species flow rate. Plotting of this quantity as a function of the activity difference gave a straight line whose slope was the permeation coefficient. While this treatment is adequate to describe the effectiveness of the sealing techniques being investigated, more detailed consideration is being applied to develop fundamental understanding of the system.

Construction was completed of the platinum-wound furnace for dynamic high temperature x-ray diffraction studies. The furnace was tested thoroughly at temperatures up to 2300° F. Performance of the furnace was very satisfactory under all test conditions. The sample temperature was held within 5° F at 2300° F. In tentative test runs, cast silica samples were heated in the furnace and continuous scans were made of the (101) plane of  $\beta$  cristobalite using copper K $\alpha$  radiation. Two of these runs are shown in Figure 4 together with a run by Verduch (J. Am. Ceram. Soc. 41 427ff, November 1958) for comparison purposes.

Efforts to determine the nature of bonding in the silica were continued using optical and electron microscopy. With optical microscopy, difficulties were encountered from the low contrast of the white particles. The contrast was improved to the point of allowing satisfactory examination at 600X by dyeing with an ordinary blue ink. Better results were obtained by using a monochromatic light source to illuminate a silica sample shadowed at a low angle with aluminum. Electron microscopy has been continued using replica techniques on sawed and broken samples. Extensive investigation has been deferred pending development of a suitable polishing technique which would enable the point particle-bonding areas to be observed.

## II. Future Work

Attempts will be pursued to develop a more satisfactory sample configuration for determining high temperature tensile strengths.

Permeation studies will be continued using discs subjected to different firing conditions and discs sealed with ethyl silicate 40, tetraethyl orthosilicate, and aluminum phosphate.

Firing studies will be initiated to determine the influence of the above sealing materials on the strength of slip-cast fused silica.

Studies of the kinetics of cristobalite growth in silica will be continued in the high temperature x-ray camera.

Reactor Division  
Oak Ridge Operations Office

-3-

July 21, 1959

Further investigations will be made of the application of optical and electron microscopy to the fused silica system.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

✓ J. D. Walton, Head  
Ceramic Branch

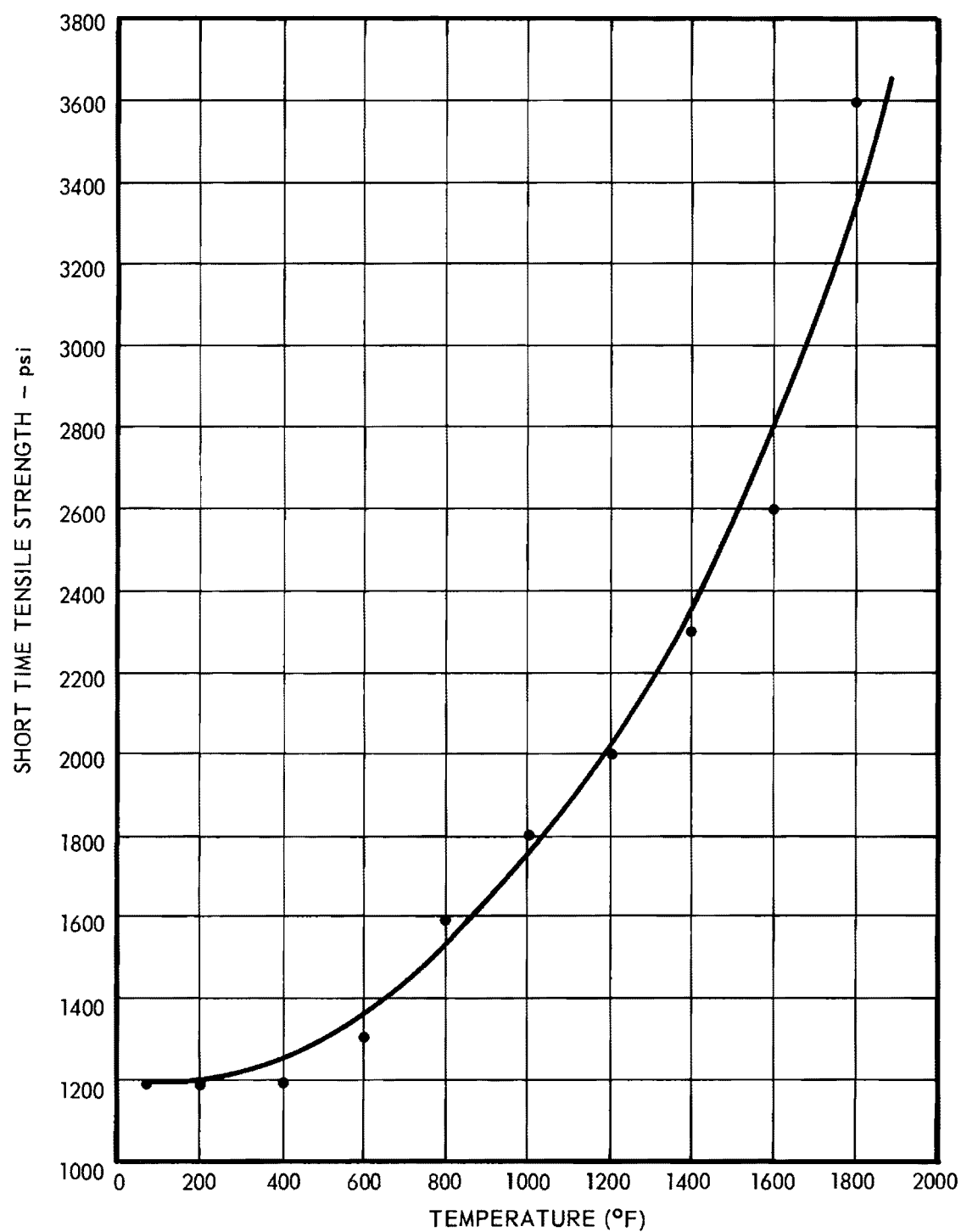


Figure 1. Tensile Strength of Slip Cast Fused Silica as a Function of Temperature.

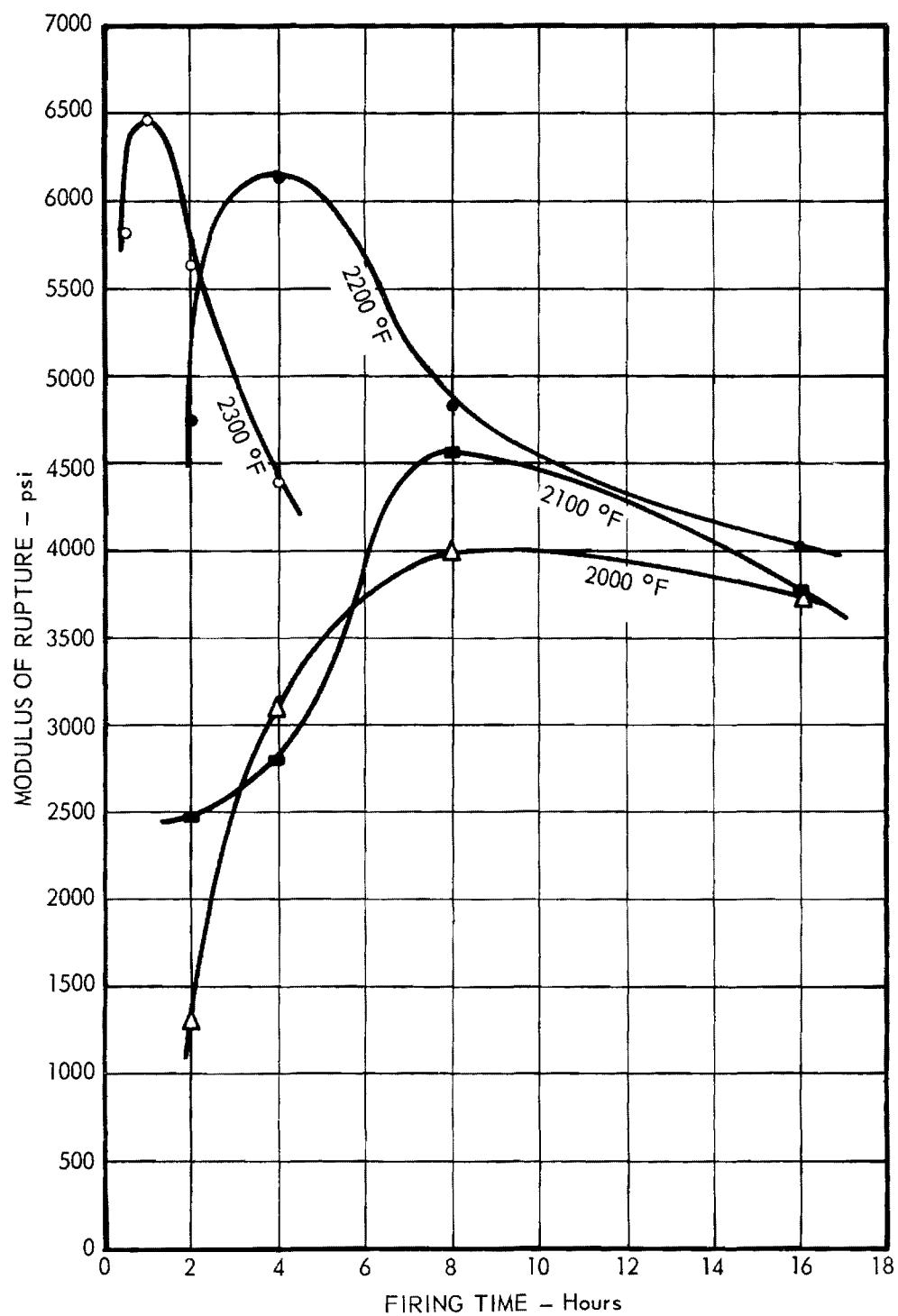


Figure 2. Modulus of Rupture of Slip Cast Fused Silica as a Function of Time at Constant Firing Temperature.

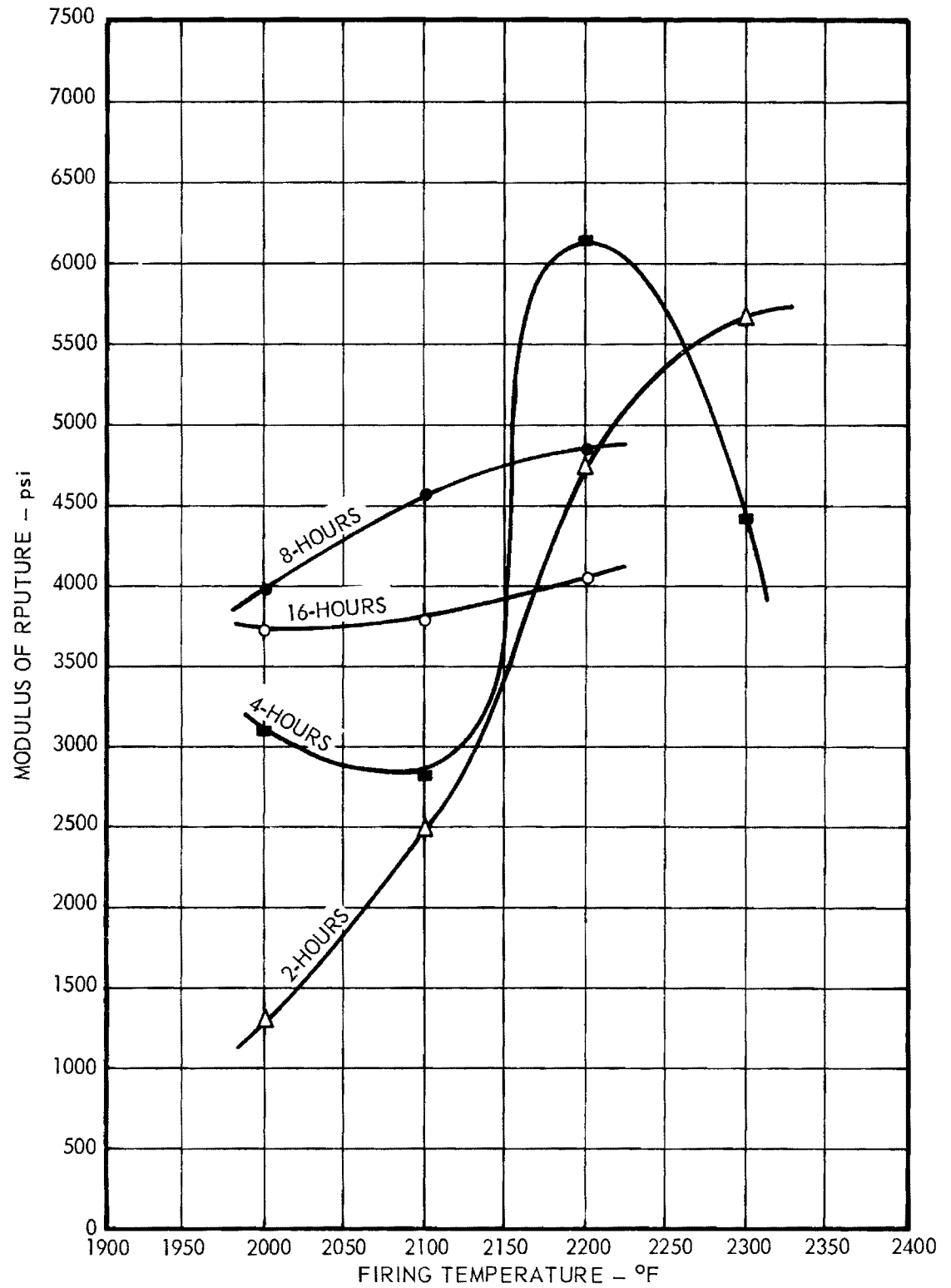


Figure 3. Modulus of Rupture of Slip Cast Fused Silica as a Function of Firing Temperature at Constant Firing Time.

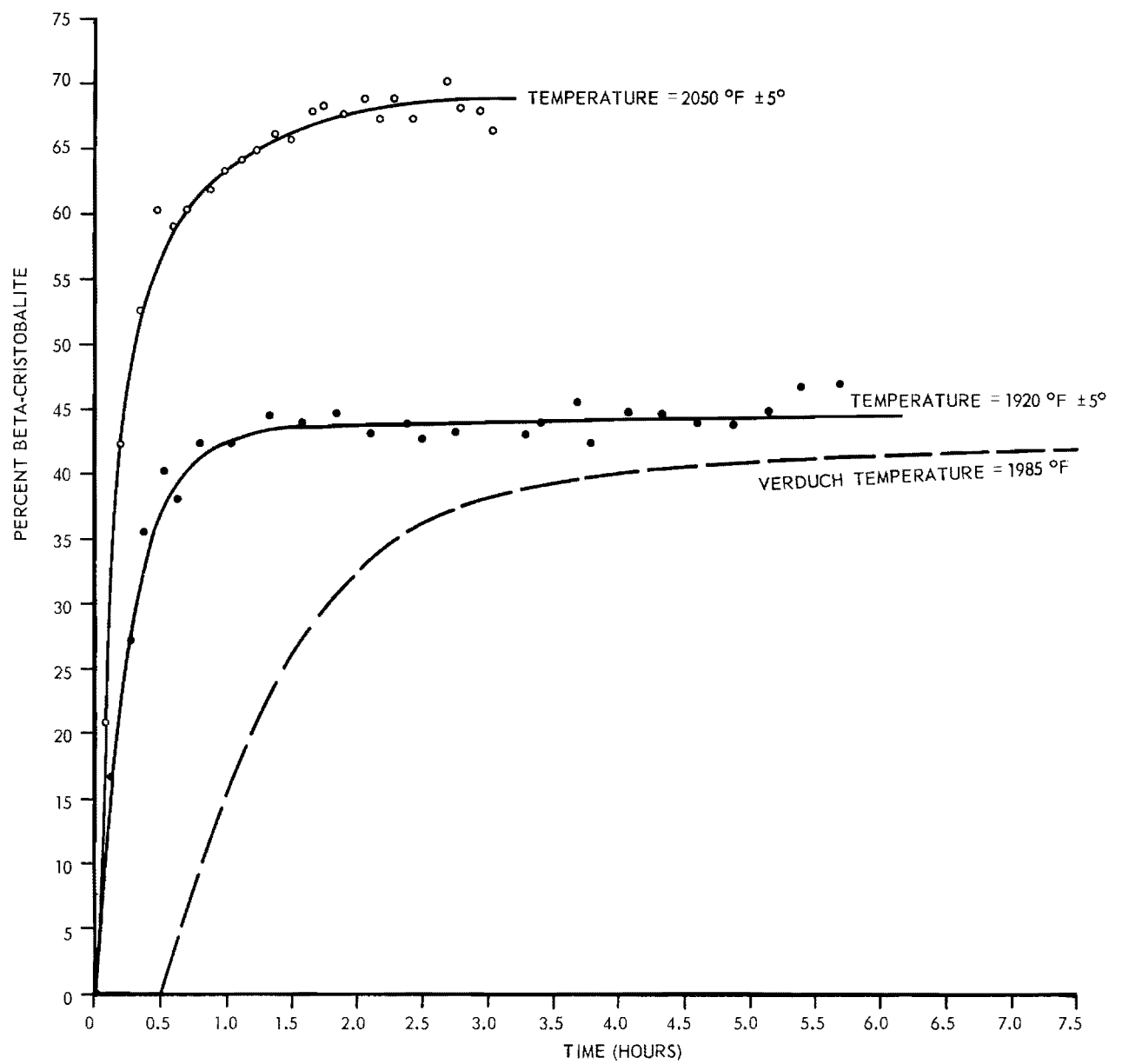


Figure 4. The Growth of Beta-Cristobalite in Slip Cast Fused Silica.

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

August 25, 1959



Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject : Monthly Letter Report No. 9, Project No. B-153  
Covering the Period from 15 July to 15 August 1959  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

✓  
Efforts to overcome end breaks in the threaded specimens have been largely ineffective. In the interest of time, a smaller sample of the B configuration (see Summary Report No. 1) was cast in the usual manner. These specimens, referred to as D tensile test specimens, could be used with the threaded Inconel holding fixtures by means of graphite or Inconel ring adapters. Tests were begun to determine the suitability of such a configuration. In room temperature tests, the samples fractured at the reduced area and appeared quite satisfactory.

The poor results obtained in the past with commercial and custom fabricated wire-wound furnaces for the tensile tester have prompted the development of a more stable furnace. Tubular forms are being cast to contain mixtures of carbon and silicon carbide granules which will serve as electrical resistance heaters. Tests of prototypes of these furnaces have provided very uniform, easily controlled heating to about 2600°F with every indication of stability.

Studies were begun to determine the influence on strength of soaking the cast silica in tetraethyl orthosilicate and ethyl silicate 40 and firing to deposit silica. In order to establish standard soaking procedures, a series of tests was made to determine the time required for the soaking solutions to gel. Mixtures of the tetraethyl orthosilicate and ethyl silicate 40 which gel in 16 hours contain 18.0 and 18.7 per cent available SiO<sub>2</sub> respectively. In view of the close correspondence of these values, 16 hour gelling mixtures will be used and the soaking will be continued until gelling occurs. In later studies, the influence of gelling time on the strength of the fired bars will be determined.

Investigations were begun to determine the influence of firing conditions on the permeation coefficients for krypton flow through silica. Firings are to be made at 2000, 2100, 2200, and 2300°F for periods of time from 2 to 16 hours. The porosities of the discs are measured prior to testing. Tentative results indicate a definite trend for the change in permeation coefficient with porosity but insufficient data have been obtained to draw a reliable correlation.

Devitrification runs were continued in the platinum wound high temperature x-ray attachment. Since platinum was evaporated onto the sample from the furnace in amounts sufficient to decrease the intensities of the x-ray beam, a correction experiment was run. Films of platinum were deposited onto silica samples by cathode sputtering techniques and their thicknesses were determined from interferometry and micro-weighing techniques. Diffraction runs on these samples permitted calibration curves of intensity vs. film thickness to be drawn. From these curves and the peak heights of the platinum traces taken during the devitrification runs, corrections could be made to the peak heights of cristobalite to account for the platinum masking effects. Using this technique, runs were begun at 50°F intervals from 1700°F to 2300°F.

Investigations were continued of the observation of the bonding regions of the cast silica using electron microscopy. Although concrete results have not yet been obtained, two techniques appear to show promise. Powder made by crushing fired silica bodies seems to retain sufficient numbers of bonded particles to afford regions in which direct observation of the bonded zone may be made. Particles are also stripped off the sample along with plastic replicas and can be subjected to direct examination.

## II. Future Work

Upon fabrication of a suitable testing furnace, the smaller D test specimens will be tensile tested at elevated temperatures.

A firing jig for D specimens will be made and studies will be initiated to determine concretely the effect of firing conditions on the tensile strengths of the cast fused silica. The jig will control the position of the test specimens in the firing chamber and will include temperature monitors.

Permeation studies will be continued to determine the influence of firing and soaking conditions on the gas-tightness of the silica.

Firing studies will be continued to determine the influence of soaking in the organosilicates on the strength of the cast silica.

Studies of the kinetics of cristobalite growth in cast fused silica will be continued in the high temperature x-ray camera.



Reactor Division  
Oak Ridge Operations Office

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August 25, 1959

Investigations will be continued to determine the possibilities for direct electron microscope examination of the cast fused silica.

Respectfully submitted:  
^

*D.* D. Fleming  
Senior Investigator >

Approved:

*J.* J. D. Walton, Head  
Ceramics Branch

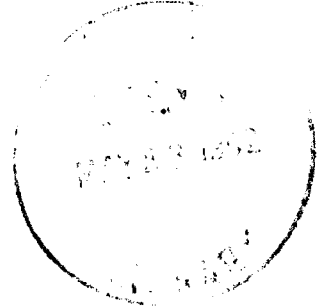
# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

September 22, 1959

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee



Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 10, Project No. B-153  
Covering the Period from 15 August to 15 September 1959  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

✓ Major emphasis, during the past report period, was placed on completing the capsules for the WTR Irradiation. The first test run will be used to determine the rate of vitrification of cristobalite and the change in strength of the slip cast fused silica under neutron irradiation.

A series of 3/8-inch bars was cast from the standard slip and fired at 2500°F for 48 hours to assure extensive cristobalite formation. Each bar was cut into two 1 1/4-inch and one 1/2-inch lengths. X-ray diffraction patterns were made on opposite sides of the longer bars to determine the cristobalite content at the surface. The shorter length was crushed and analyzed for bulk cristobalite content. Following the x-ray analyses, the 1 1/4-inch lengths were sealed in the irradiation capsules so that two bars will be placed in each axial position in the reactor basket. If the reactor is operated at the anticipated power level of 20 mw, the samples should receive doses ranging approximately from 1 to  $8 \times 10^{20}$  nvt. Following the irradiation, the bars will again be analyzed for the surface cristobalite content and then crushed for bulk cristobalite analysis. The pre- and post-irradiation cristobalite analyses will permit calculation of the vitrification rate as a function of neutron dosage.

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 (Figure 8, Progress Report No. 1) and had moduli of rupture of 5770, 6490,

September 22, 1959

and 5490 psi respectively. The bars were subjected to x-ray analysis for cristobalite content, both surface and bulk. Samples were sealed in the irradiation capsules in an arrangement such that the bars with higher cristobalite contents will be placed in the higher flux positions of the reactor basket and lower cristobalite bars will be placed in lower flux positions.

The use of bars fired on each side of the peak strength firing conditions should allow some conclusions to be drawn concerning the relative strengthening due to displacement of randomly arranged molecules, in the amorphous silica, and regularly arranged molecules, in the crystalline silica.

The flux at each of the irradiation capsules will be monitored with aluminum discs placed between the capsules in the sample basket. As soon as possible after the sample basket is removed from the reactor, the discs will be counted in a  $4\pi$  system with discrimination for Mg 27 and Na 24. This activation analysis should permit calculation of the neutron dosages above 4.6 mev and above 8.1 mev for each axial capsule position.

The sealed capsules and aluminum flux monitors were forwarded to the WTR for inclusion in the first testing cycle.

## II. Future Work

Studies will be resumed to determine the influence on strength of soaking fused silica in organosilicates.

Permeation studies will be continued to determine the influence of firing and soaking conditions on the gas retention properties of the cast fused silica. The sealing systems will be expanded to include carbon deposition from phenol-formaldehyde resins.

High temperature x-ray runs will be made to complete the first series of devitrification rate determinations.

The influence of firing conditions on tensile strength will be further investigated using an Inconel firing chamber.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

APPROVED:

J. D. Walton, Head  
Ceramics Branch

15-12-59

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

October 22, 1959

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 11, Project No. B-153  
Covering the Period from 15 September to 15 October 1959  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

✓ Firings were begun of the D tensile test specimens with 1/4-inch minimum diameter. An initial series of 15 specimens was dried and fired at 2200°F for four hours in the tube furnace described in previous reports. The samples were tested at room temperature using the Inconel holding fixtures. The average tensile strength was 1960 psi with maximum and minimum values of 3150 psi and 1020 psi respectively and an average deviation of 23.5 per cent.

The first 1 3/4-inch diameter, 6-inch long testing furnace for elevated temperature tensile testing was completed. The furnace shell and tube were cast from silica and silica foam was used as insulation. The furnace heating space was filled with a tamped mixture of 50 per cent flake graphite and 50 per cent 320 grit silicon carbide. Power was furnished to the furnace at 30 volts by a step down transformer controlled by a Variac. A power input of approximately 1.5 kva was sufficient to heat the furnace to 2400°F in about two hours. Since silica was used as the furnace structural material and since granular graphite-silicon carbide served as the resistance heating element, no attempt was necessary to avoid thermal shock through rapid heating. The full line power was applied to the cold furnace and heating was allowed to proceed as rapidly as possible. The furnace appeared most satisfactory and will be used for all elevated temperature tests unless unforeseen difficulties arise. Since the cost of fabricating an entirely new furnace is less than twenty dollars, the furnace will simply be replaced if fracture occurs through devitrification of the silica.

Studies were resumed to determine the influence, on strength, of soaking techniques intended to seal the porous silica. Difficulty was encountered in fabricating a large enough series of transverse test specimens with reproducible moduli of rupture. In one attempt to decrease the variation in moduli of rupture caused by nonreproducible factors in the testing system, a modification of the Dillon tester was begun to permit four point, rather than three point, loading.

October 22, 1959

The large deviations observed in both modulus of rupture and tensile strength indicated that some fabrication or firing variable was being inadequately controlled. In order to determine the best sample preparation technique, a statistical analysis was begun of firing methods. A series of bars will be fired in the tube furnace and in shielded enclosures in muffle furnaces. Enough samples will be used to yield a reliable comparison of variance and standard deviation for the different firing techniques. From this analysis, the most reproducible firing technique will be selected for future use.

In addition to the analysis of firing technique, attempts will be made to obtain plaster which will produce molds of more uniform and reproducible permeability. Reports have been received of a new plaster from the Bestwall Company which is reputed to be considerably more uniform in properties than the conventional plaster used in the previous studies.

Permeation runs were continued at room temperature.

The first series of dynamic x-ray diffraction studies of the silica devitrification kinetics was completed. Analysis of the results was begun.

## II. Future Work

Studies will be continued to determine the influence of firing conditions on the tensile strength of the slip cast silica.

Elevated temperature tensile testing will be begun using the cast silica furnace.

Permeation runs will continue.

Statistical analysis of the various techniques for firing the silica will be completed. Based on this analysis, a standard firing method will be chosen.

Analysis of the high temperature x-ray diffraction data will be continued.

Respectfully submitted,

✓  
J. D. Fleming  
Senior Investigator

Approved:

○ J. D. Walton, *J.D.*, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

November 25, 1959



Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 12, Project No. B-153  
Covering the Period from 15 October to 15 November 1959  
Contract No. AT-(40-1)-2483

Gentlemen:

✓✓  
I. Experimental Progress

Tentative test firings of the 1/4-inch diameter D tensile test specimens were continued. The samples were suspended from notched refractory supports to suppress warping and fired in a large bottom loading Globar furnace. Firings were made at a temperature of 2200° F for times of 2, 4, and 8 hours. The first firings showed somewhat higher tensile strengths than those obtained in previous firings with the 1/2-inch specimens. Within the limits of the average deviations observed, the 1/4-inch bars were 80 per cent stronger than the 1/2-inch bars reported in Progress Report No. 1, Figure 4. The smaller bars, as would be expected, showed a greater deviation than the larger bars, averaging about 25 per cent. The great difference between the large and small tensile test specimens prompted a more thorough comparison of the two types. Firings of both sizes were begun for comparison over a wide range of firing variables.

Operational testing was begun of the elevated temperature tensile testing system. A cast silica furnace, described in Monthly Letter Report No. 11, was tested to 2500° F. Heating to this temperature required 30 minutes at a power consumption of 2 kva. Several 1/4-inch tensile test specimens were broken at 2150° F with no difficulty. For a firing time of 8 hours at 2200° F, a tensile strength of approximately 5000 psi was noted at the testing temperature of 2150° F. Although the number of elevated temperature tests is insufficient for statistical reliability, the first test runs indicated that the tensile strength at 2150° F is at least double the corresponding room temperature strength.

25 November 1959

Firings were completed for the statistical study of firing procedures. Analysis of the test results was begun.

Casting rate studies were begun using both U. S. Gypsum No. 1 and Bestwall K-59 pottery plasters. The U. S. Gypsum plaster was found to give a higher casting rate for the first few minutes of casting. For the times normally used in casting large objects, however, the average casting rate was higher for the Bestwall plaster. Higher casting rates are obviously desirable in that the smaller degree of sedimentation resulting should yield more uniform test bars. Studies were begun to compare the moduli of rupture of test bars cast in the two plasters.

Differential thermal analysis investigations were continued as an alternate method of cristobalite analysis. Tentative results showed that a discernible transition peak will be given by cristobalite contents in excess of approximately 40 per cent. Studies were begun to compare the reproducibility of x-ray and DTA analyses for cristobalite.

In order to decrease the delay involved in reaching the expanded rate of effort expected for the next contract year, preliminary design calculations were begun for the test systems which will be required. Tentative designs were drawn for the high temperature hydraulic ring tensile testing system and for a supplementary differential thermal analysis system.


## II. Future Work

Studies will be continued for the determination of the influence of specimen size on tensile strength.


Elevated temperature tensile testing will be continued using a large enough sampling to permit statistical evaluation of the results.

Major attention will be devoted to organizing the new areas of effort outlined in the renewal proposal submitted under this contract.

Respectfully submitted,

 J. D. Fleming  
Senior Investigator

Approved:

 J. D. Walton, Head  
Ceramics Branch

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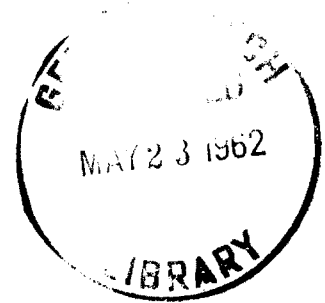
# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

December 28, 1959

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee



Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 13, Project No. B-153 Covering the  
Period from 15 November to 15 December 1959  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Design was completed for the apparatus for the ring tensile test developed by the Armour Research Foundation<sup>1</sup>. This apparatus will consist of a hydraulic system powered by a variable rate pump, a stainless steel or inconel working piston, graphite or silicon carbide compression fixtures, and a Kanthal wound furnace with suitable steel superstructure to support the necessary loads. The applied load will be recorded on a strip chart recorder using the output from a Baldwin SR-4 pressure cell tapped directly into the hydraulic cylinder. The system will be designed for a maximum working pressure of 1000 psi and will be capable of applying the maximum load in from one to five minutes.

Fabrication studies were continued in the slip casting of silica rings for tensile testing. The primary 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 and silica cores, both of which proved satisfactory. Slip cast silica cores were finally selected for routine use as a result of their better abrasion resistance finish and because economical mass production of cores by casting was possible. The use of silica cores and plaster outer molds appears to permit routine fabrication of ring tensile specimens.

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<sup>1</sup>Bortz, S. A. "A Tension Test for Brittle Materials", Appendix 3, Progress Report No. 2, Project No. G-039, Armour Research Foundation, Chicago, Illinois.



Determination of the elevated temperature tensile strength of the slip cast silica was continued using the small D specimens. Testing temperatures were reached using cast silica furnaces described in previous reports. Specimens were fired at 2200° F for 2, 4 and 8 hours and preliminary tensile tests were begun at room temperature and 1000, 1500, 2000, and 2200° F. A minimum of seven specimens will be broken at each testing temperature for each of the three firing conditions. These tests are approximately 50 per cent completed.

Statistical analysis of the data from the firing studies using silica was continued.

Both differential thermal analysis and dilatometer studies were completed using cast silica samples containing varying amounts of cristobalite. Analysis of the data was begun to obtain correlations of thermal expansion and inversion temperature with firing conditions for the slip cast fused silica.

Construction was begun of a vacuum system for the deposition of thin films of silica. These films will be used in the observation of devitrification of fused silica in the electron microscope.

Casting studies were initiated to determine the feasibility of fabricating very thin samples of silica. These samples will be required for transmission x-ray diffraction designed to detect possible preferential crystal orientation during firing and devitrification. Production of fired sheets less than one millimeter thick was found possible although warping during firing was prevalent.

The irradiated silica samples were removed from the Westinghouse Testing Reactor and transferred to a water canal. Following decay of the activity in the aluminum containment capsules, the samples will be removed and subjected to the planned x-ray and physical testing.

## II. Future Work

Upon receipt of the uranium dioxide, formulation and testing of the beryllium reductant thermets will begin. Design and construction of a suitable hooded, inert atmosphere, differential thermal analysis system will be begun.

Techniques will be developed for the deposition of silica films for electron microscopy.

The statistical study of firing methods for the slip cast silica will be completed.

The tensile strength determinations using D specimens will continue.

Respectfully submitted,

Approved:                    n

J. D. Walton, Head  
Ceramics Branch

J. D. Fleming  
Senior Investigator

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

January 25, 1960

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 14, Project No. B-153  
Covering the Period from 15 December 1959 to 15 January 1960  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

With the receipt of Davison ceramic grade uranium dioxide and Brush beryllium, the exploratory investigation of beryllium-uranium dioxide thermets was begun. The reactants were mixed in stoichiometric proportions according to the basic thermet reaction



$$\Delta F_{298} = -24.7 \text{ kcal}$$

Fabrication was begun of differential thermal analysis (DTA) pellets of this mixture using water as a lubricant. Pellets will be pressed at combinations of three pressures and four lubricant percentages. DTA curves will be run on these pellets at 10 and 20° F/min. temperature increase rates to determine the ignition temperatures.

Design was completed and equipment was ordered for a hooded, inert atmosphere DTA system to supplement existing facilities and permit rapid evaluation of the thermets.

Elevated temperature tensile tests were continued using the small D specimens. Samples were cast and fired at 2200° F for periods of 2, 4, and 8 hours. Tensile tests were then made at temperatures of 1000, 1500, and 2000° F. An increase in strength with temperature was noted in all cases. The strength seemed to approach a value of about 4100 psi at 2000° F regardless of the firing treatment used. Insufficient data are available to quantitatively confirm this observation. Further elevated temperature tests will be slowed until construction of the ring tensile testing apparatus is completed.

Room temperature tensile tests were carried out to determine the influence of firing conditions on strength. Because the small D sample configuration used permitted firing free of warping, higher strengths were noted than were previously obtained with the large D specimens. In the first tests, using firing temperatures of 2200° F, a curve was obtained which was parallel to that of Figure 4, Progress Report No. 1, but displaced to strengths about 65 per cent higher.

Work was begun on the adaptation of the graphite mold release developed at Los Alamos<sup>1</sup> to an aqueous system. Dixon's No. 635 flake graphite was milled and suspended in a variety of polar media. Casting studies were begun with these suspensions being used to form graphite mold coatings.

The statistical study of fabrication variables was completed. In order to make the preliminary survey as simple and convenient as possible, the variables considered were limited to three, the mold, the slip, and the firing conditions including temperature and time. A standard statistical analysis of the transverse strengths was carried out in which calculations were made of the mean square due to each individual variable and 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. The condition and manipulation of the mold did not significantly influence the strength since its mean square was only 390, 637 compared to an error variance of 229, 470. Both the nature of the slip and the firing conditions influenced the strength as indicated by mean squares of 3,174,337 and 2,552,420 respectively. This represents significance at the 0.1 per cent level compared to the 5 per cent level usually considered real from a statistical viewpoint. The study showed an insignificant influence of casting technique on fired strength. This observation is of extreme importance in the evaluation of sealing additives now underway as well as in implying that comparable results should be obtained by different investigators using the same slip and firing conditions.

The silica samples which were irradiated in the WTR were de-encapsulated and are in transit to Georgia Tech. Pending analysis of the reactor power history during the run, the average dose has been estimated as about  $1.5 \times 10^{20}$  nvt. No change in the silica was apparent from outside the hot cell. Activation of the silica was very slight, resulting in only about  $10^6$  dps of Zn-65 activity per gram.

## II. Future Work

Determinations of the ignition temperatures of beryllium-uranium dioxide thermets will be begun.

Tensile strength determinations, both room and elevated temperature, will be continued.

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<sup>1</sup>Private communication with R. E. Cowan, S. D. Stoddard, and D. E. Nuckolls, Los Alamos Scientific Laboratory; CMB Division.

Reactor Division  
Oak Ridge Operations Office

-3-

January 25, 1960

Upon receipt of the irradiated silica specimens, the proposed physical testing and x-ray determinations will be made.

Preliminary design considerations will be begun for motion micrography of slip casting systems.

Design calculations will be made for the test capsule to be used in the 2000° F irradiation of silica planned for October, 1960.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

February 19, 1960

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 15, Project No. B-153  
Covering the Period from 15 January to 15 February 1960  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

The irradiated silica samples were received from the WTR. The average fast neutron ( $>0.8$  mev) dose received by the samples was  $1.5 \times 10^{20}$  nvt. The samples were unchanged in physical appearance and size by the irradiation. Transverse strength measurements were made on the irradiated bars and on unirradiated bars retained from the same fired groups. A detailed statistical analysis of the data is underway to attempt to obtain a quantitative evaluation of the influence of irradiation on the strength of the slip cast fused silica. Preliminary evaluation of the data indicated that the strength of the silica was not significantly changed in any way by the irradiation.

X-ray diffraction analysis of the irradiated silica was begun. Initial examinations of bars which were almost totally devitrified prior to irradiation showed evidence of total destruction of the cristobalite. In these bars no structural change or gross failure was noted. No tendency was observed for microcracks in the silica to heal under irradiation since the strengths of these samples remained characteristically low.

Initial test firings were made of simple beryllium-uranium dioxide thermets to ensure absence of handling hazards. DTA pellets were pressed at 20,000 psi using 10 per cent water as a lubricant. Several of these pellets were fired in air and in argon. Upon reaching a temperature of approximately  $1700^{\circ}$  F, the pellets ignited and rapidly reached a bright white heat. During the air firings the pellets began oxidizing and crumbled following the reaction. The pellets showed no tendency to oxidize during the reaction, indicating that subsequent oxidation of the uranium formed in the reaction probably accounted for the eventual decomposition of the pellets. Pellets fired and cooled in argon remained intact and did not undergo warping during the reaction. Several

February 19, 1960

pellets were sectioned with a diamond saw and given brief microscopic examinations. The structure appeared quite dense and free of blow holes. The pellets were quite easy to saw and did not splinter or fragment.

Investigations of graphite mold release suspensions were continued. Suspensions of milled graphite in methanol and ethanol were found to give satisfactory results. Bars cast using graphite as the releasing agent were easier to remove from the mold than bars cast using Keltex. The Keltex released bars did show a lesser tendency to break during prefiring handling because of the support afforded the green bar by the Keltex film. In addition, the graphite released bars seemed to have a less smooth surface finish. Comparisons of casting rates were begun with both releasing agents.

Data were received from WTR and design calculations were begun for the instrumented capsule to be irradiated at elevated temperatures. Feasibility studies were begun of wire wound and sprayed conductor resistance heaters for the test capsule.

## II. Future Work

Optimum pressure and lubricant ranges will be determined for the beryllium-uranium dioxide thermets. Following this study, DTA firings will be begun.

Tensile strength determinations will be continued.

Design of systems for motion and hot stage microscopy will be continued.

Further design studies will be made in the development of the elevated temperature irradiation capsule.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

March 25, 1960

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 16, Project No. B-153  
Covering the Period from 15 February to 15 March 1960  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Testing of the irradiated silica bars was continued. Considerable trouble was encountered from free surface contamination on the samples. Rough experiments proved that the contamination was external to the silica, possibly resulting from handling inside a contaminated hot cell. The majority of the free contaminant, a weak beta emitter, could be removed by acid rinsing of the samples. No detailed attempt was made to identify the contaminant since it did not arise from the silica itself. Completion of the testing program will be delayed until the samples can be completely decontaminated.

Statistical analysis of the transverse strength of the irradiated silica samples was completed. In each case, the average transverse strength was slightly lower ( $\sim 10$  o/o) for the irradiated samples than for non-irradiated silica. Since the number of irradiated samples was small, the transverse strengths of irradiated and non-irradiated samples were carefully compared to determine the degree of statistical significance of this strength decrease. 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. From the viewpoint of statistical validity then, the irradiation to  $1.5 \times 10^{20}$  nvt cannot be said to have caused a change in the strength of the silica.

Samples of the silica were cast in the configuration for the Armour ring test (see Monthly Report No. 13) and forwarded to Armour for testing. Six ring samples of silica fired at  $2200^{\circ}$  F for 4 hours were tested at room temperature. These samples gave an average tensile strength of 3260 psi. A series of small D configuration specimens, prepared at the same time as the ring samples, gave an average tensile strength of 3250 psi. The agreement between the two methods will be more extensively explored following completion of the ring tester but shows promise of allowing the more simple ring test to be used for elevated temperature testing.

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Detailed studies were continued to determine the optimum plaster and plaster condition for silica casting. A comparison of Gypsum No. 1 plaster and Puritan plaster showed a slightly faster casting rate and slightly stronger castings for the Puritan plaster. The uniformity of the Puritan plaster also seemed significantly better than the No. 1.

Initial DTA runs were made with the pressed Be-UO<sub>2</sub> thermet mixture. Ignition was found to occur at about 400° F in contrast to the rough observation of 1700° F made in previous work. No explanation for this anomalous behavior has been found. More detailed work was begun, with increased safety precautions, to further explore the firing process.

After detailed evaluation of optical hot stage designs, in consideration of economy a commercial unit was chosen rather than attempting to construct a special system. This commercial stage manufactured by Unitron is capable of 1500° C operation and should be well suited to the casting investigations.

Concurrent design studies were begun for hot stages for the RCA EMU-2 and Philips EM-100. Both systems will be evaluated and the simpler stage will be used in all hot stage work.

Development was continued for the heated capsule for the WTR irradiation study.

## II. Future Work

Tensile strength determinations will be continued.

DTA firings of the UO<sub>2</sub> - Be thermets will be emphasized. Firings in inert atmospheres will be attempted.

Construction of electron microscope hot stage prototypes will be begun.

Comparison of casting plasters will be completed.

Systems development will be continued for motion microscopy and the heated irradiation capsule.

Respectfully submitted,

✓ J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch



# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

April 26, 1960

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 17, Project No. B-153  
Covering the Period from 15 March to 15 April 1960  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

In order to establish an absolute standard for future correlation of the x-ray studies, attempts were begun to prepare a completely crystallized cristobalite sample. Slip cast bars were fired for long periods of time at high temperatures, ground, and analyzed for the cristobalite diffraction peak area. Following examination, the powder was suspended in a bromoethane-methanol mixture with a density of 2.26, halfway between the densities of fused silica and cristobalite. The cristobalite-rich sediment was separated, dried, and re-analyzed for the cristobalite peak. Difficulty with evaporation and density drift in the flotation medium prevented accurate separation. A closed flotation system is to be used in order to avoid evaporation and the concomitant density drift. As a further purification step, following flotation, an investigation was begun of selective leaching of the amorphous silica using hydrofluoric acid.

Standards were prepared for x-ray fluorescence determinations of the surface composition of silica slip cast in different molds. These standards, varying from 0.0001 to 5.0 per cent of 43 elements, will permit analysis of the impurities absorbed from the plaster molds during slip casting. Comparisons will be made of the surface contamination of the silica resulting from casting in plaster and in silica molds.

Work was begun on developing a more suitable furnace for the high temperature x-ray diffraction camera. A method for determining the thickness of platinum films by x-ray fluorescence was developed in case the use of exposed platinum heating elements continues to be necessary. This procedure appears to be considerably more accurate than the interference methods previously used.

Preliminary investigations were begun to determine the crystallization mechanics of amorphous silica. Several fused silica glass samples were partially devitrified and examined for crystallite orientation by x-ray diffraction. In all cases, a marked orientation of the (101) cristobalite planes was noted to

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occur parallel to the sample surfaces. The firing method was seen to affect the orientation to some extent, but the intensity variation was invariably 50 to 100 per cent greater for the (101) pole. Fused silica plates with a flat surface finish are being obtained to permit greater precision in the x-ray investigation.

Several microscopy techniques were studied for use in observing the slip casting behavior of silica. A combination of transmitted and reflected light, obtained with Ultrapak attachments, revealed the motion of the silica particles during casting with startling clarity. The same system also showed promise of permitting observation of the drying behavior of the cast slip. Attempts were begun to take motion pictures of the casting and drying process using this microscope arrangement.

The thermet pellets produced from the Be- $\text{UO}_2$  reaction were mounted and polished for metallographic examination. Particles of distinctly metallic appearance were noted in most cases. X-ray diffraction has proved incapable of analyzing the reaction products, presumably because the mixture consists of the very light beryllium and very heavy uranium. Selected area electron diffraction patterns have been taken on particles stripped from the thermetts with polyvinyl alcohol. Collection of patterns from the pure  $\text{UO}_2$ , BeO, and Be on hand was begun. The patterns from the thermetts have not corresponded with the pure material patterns taken to date.

An annealing study was carried out to determine the possibility of increasing the strength of the slip cast silica by heat treatment. No improvement was noted over the process of post-firing quenching whether the silica was cooled slowly or reheated.

## II. Future Work

The DTA system for inert gas firing will be completed. Firing of the  $\text{UO}_2$  - Be thermetts will then be carried out under controlled conditions.

Development of systems for motion microscopy will be continued.

High temperature crystallization kinetics will be further explored.

The phenomenon of preferred crystal orientation in devitrification will be investigated.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

May 25, 1960

## REVIEW

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

PATENT 7-19 1960 BY.....  
FORMAT ..... 19..... BY.....

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 18, Project No. B-153  
Covering the Period from 15 April to 15 May 1960  
Contract No. AT-(40-1)-2483

Gentlemen:

### I. Experimental Progress

The remaining equipment and instrumentation for the high temperature ring tensile tester were received. Construction of the furnace and loading system was completed. Construction of the control panel was begun. Studies were carried out in the development of a new mold design for the ring samples. Satisfactory castings are being produced from closed two piece molds having a central passageway for a brass core and two pouring spouts parallel to the axis of the core.

Construction was completed on the vacuum system for deposition of the thin silica films. A heated substrate holder was designed for inclusion in the system. The heater will permit outgassing of the substrate and control of the substrate temperature during film deposition.

The inert gas DTA system was completed. The system differs from conventional systems in that two standard pellets are used, one for comparison with the unknown and one for control of the heating rate. Designed heating rates cover the range from 5 to 120°F per minute. Although immediate use of the higher rates is not anticipated, thermal shock of the furnace body should not be a limiting factor since fused silica was used exclusively in the construction of the furnace. Standardization of the system controls was begun. Some difficulty was experienced through malfunction of the cam heating rate control. Modification of the control was begun to eliminate these difficulties.

A test prototype of a recording thermogravimetric balance was built and tested. The system proved stable in operation. Check runs were carried out using UO<sub>2</sub>-Be thermite pellets fired in air. The firing point of the pellets used was found to be approximately 450°F in air or argon as determined by DTA.

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Thermogravimetric firings were carried out 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 uranium dioxide, initially  $\text{UO}_{2.04}$ , to  $\text{UO}_{2.06}$  could be detected. No weight change was found to occur during the firing of the thermets or to occur prior to a post-firing temperature of approximately  $600^{\circ}\text{F}$ . At  $600^{\circ}\text{F}$  a weight gain of 3.4 per cent was detected following which the pellet crumbled and was partially lost from the weighing capsule. Preliminary support was thus obtained for the suggestion of an initial reduction of the uranium dioxide followed by re-oxidation of the metallic uranium generated during the reduction.

X-ray fluorescence determinations were made of the surface contamination resulting from casting in plaster molds. Samples were cast in three types of plaster using Keltex as the mold release agent. The calcium content of the samples fired with the Keltex film in place was found to be an order of magnitude higher than that of samples fired following stripping of the Keltex film. Since calcium is known to accelerate the devitrification of silica, as well as generate undesirable activity under irradiation, efforts were begun to avoid its deposition on the sample surface.

A procedure was developed which will allow motion micrography of the silica during slip casting. Initial work will utilize a camera speed of 128 frames per second although Fastax photography is available if necessary. Illumination of the casting slip will utilize a controlled combination of transmitted and reflected light.

Design calculations were completed for the heated irradiation capsule to be used in the studies of neutron damage of silica at elevated temperatures in the WTR. These calculations indicated that much of the necessary heat input to the silica can be furnished by gamma absorption. These calculations show a need for modification of the irradiation schedule previously planned. These modifications are fully discussed and submitted for approval in Special Report No. 1 under the subject contract.

## II. Future Work

Construction of the ring tensile testing system will be continued.

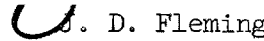
Checkout and required modifications of the inert atmosphere DTA system will be completed. Test firings of the  $\text{UO}_2$ -Be thermets will be begun.


Provisions will be made for inert atmosphere thermogravimetric firing of the thermets.

Construction will be begun of the heated stage prototype for the RCA EMU-2 electron microscope.

Respectfully submitted,

Approved:

 U. D. Fleming  
Senior Investigator

 J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

June 21, 1960

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 19, Project No. B-153  
Covering the Period from 15 May to 15 June 1960  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Construction of the high temperature ring tensile tester was completed. Initial attempts to control the sample loading rate proved unsuccessful using only the single stage flow control valve. A second regulating valve was ordered for the hydraulic system.

A systematic study was completed to determine the influence of plaster type and composition on the strength of the slip cast fused silica. Molds were made of three plaster compositions using U. S. Gypsum No. 1 and Puritan and Bestwall K-55 plasters. The molds were conditioned and two groups of castings were made in each. The bars were fired randomly in nine groups of 40 bars each for four hours at 2200°F. Although detailed statistical analysis of the data is not yet complete, it appears that the bars cast in the three plasters were equally strong.

Work was continued in the development of a graphite mold release. Suspensions produced by co-milling graphite and gum arabic in water have proved most satisfactory. A series of castings was made using Keltex

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releasing agent and the milled graphite suspension. The bars were fired at 2200°F for four hours. The average transverse strength of the bars cast using the graphite release was 5940 psi, almost 20 per cent greater than the average strength of the bars cast using Keltex. Casting times for the graphite release were approximately 20 per cent shorter.

Preliminary studies were made of techniques for permeating the silica with ethyl silicate. A system was designed and constructed for maintaining a vacuum on the silica being soaked and pressure on the soaking liquid. Using this apparatus, saturation of a six inch transverse bar proved possible in two hours. Bars were cast for a full study of the influence of the soaking on the strength of the silica.

Studies were continued of the movement of silica particles during slip casting. Motion pictures were made using a Leitz binocular microscope with a Homal II ocular and a 32X objective at a total magnification of about 250X. The pictures were made at 64 frames per second with a Kodak Cine' Special camera and a 40 mm lens. Kodak Tri-X reversal film with an ASA rating of 200 was used. Motion of the majority of the silica particles was clearly recorded although the small particles were indistinct. Attempts were begun to improve the resolution of the system.

Construction was begun of the prototype of the hot stage for the electron microscope.

Design of the high temperature irradiation experiment was halted pending approval of the modified approach recommended in Special Report No. 1.

## II. Future Work

Check out of the ring tensile testing apparatus will be completed. Following this check out, high temperature testing will be begun.

Further investigation of the graphite mold release will be made.

Motion microphotography of the slip casting of silica will be continued.

Phase IV of this project will be reported at a later date.

Respectfully submitted,

V. D. Fleming (/  
Senior Investigator

Approved:

7 J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

July 21, 1960

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Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope

Subject: Monthly Letter Report No. 20, Project No. B-153  
Covering the Period from 15 June to 15 July 1960  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

A precision regulating valve was installed in the hydraulic system of the ring tensile testing machine. This valve allows critical control of the hydraulic fluid flow rate so that the loading rate of the tester can be adjusted at will. The SR-4 pressure cell was calibrated using dead weight loading. A trial series of slip cast fused silica rings was run at room temperature. The loading rate used was approximately 500 pounds per minute. Clearly defined breaking load peaks were observed on the recorded load charts along with an essentially instantaneous load release upon fracture. The fracture pattern in the sample was exactly as was expected, with pyramidal fracture planes radiating from the loading point. The series of ring tests gave a room temperature strength of 3,330 psi with a maximum deviation of 14.6 per cent. These results compared quite favorably with strengths of 3,250 psi and 3,260 psi determined respectively with ordinary tensile specimens and with ring specimens tested at the Armour Research Foundation. The values determined using the usual D tensile test bars showed a maximum deviation of 37 per cent while those determined by Armour gave a maximum deviation of 24 per cent.

The furnace on the ring tester was taken to a temperature of 2200°F slowly to remove water from the brick. The furnace functioned satisfactorily. Initial check tests were begun at elevated temperatures.

Motion photomicrography was further explored using fused silica slip. The system resolution was improved considerably and optimum exposure conditions were established. Efforts were begun to increase the useful magnification and photographic resolution by the use of a Bolex camera. Evaluation of Fastax photography was begun since the particle speed at higher magnifications will probably necessitate film speeds higher than 64 frames per second.

July 21, 1960

Work was continued in the development of alumina, tungsten, and uranium dioxide slips for comparison with the fused silica slip. Alumina slips were developed which gave satisfactory castings. The total shrinkage from the master mold to a final casting fired for one hour at 3100°F was approximately 10 per cent. Fired densities approached 90 per cent of theoretical. Green moduli of rupture approached 1000 psi and moduli of rupture of bars fired for one hour at 3100°F exceeded 20,000 psi. Attempts were begun to carry out motion photomicrography using the alumina slip.

In accordance with approval received in reply to Special Report No. 1, construction was begun of the sample basket for the elevated temperature irradiation of silica. Machining of the capsule was completed using 316 stainless steel for the shell and 304 stainless steel for the plugs. Alundum aluminum oxide castable, foamed fused silica, and slip cast fused silica were studied as insulators for 15/32-inch silica samples. The temperature at several points in the capsule will be monitored with platinum sheathed, aluminum oxide insulated, platinum-platinum 13 per cent rhodium thermocouples. The irradiation will be a "maximum temperature" test using gamma heating only. Centerline sample temperatures are expected to approach 2000°F.

Work was continued with thermetic mixtures of aluminum, zirconium, beryllium, and uranium compounds. A report of this work will be delayed pending an evaluation of the security classification status of this portion of the program.

## II. Future Work

Ring tensile testing of the slip cast fused silica will be extended to higher temperatures.

Motion photomicrography will be further explored with both silica and alumina slips.

A conference will be held with WTR personnel to resolve questions concerning the irradiation program. Following the conference, formal quotations will be obtained for the irradiation.

Respectfully submitted,

✓ J. D. Fleming  
Senior Investigator

Approved:

/J. D. Walton, Head  
Ceramics Branch



# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

August 24, 1960

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Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 21, Project No. B-153  
Covering the Period from 15 July to 15 August 1960  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Tensile testing was carried out at temperatures up to 2200°F to further evaluate the ring testing system. The SR-4 pressure cell was calibrated using dead weight loading. Silica rings, fired at 2200°F for four hours, were loaded at 500 pounds per minute following an initial soaking time of approximately five minutes at temperature. At a testing temperature of 2200°F, the loading curve was linear with time, as in room temperature testing, at low stress. As the stress was increased above approximately 4000 psi, evidence of plastic deformation of the silica was given by a deviation of the loading curve from linearity. The departure from linearity increased with increasing stress. Fracture of the sample finally occurred at an apparent stress of approximately 8000 psi. Upon removal of the sample from the testing chamber and reassembly of the fractured parts, the ring was seen to have been plastically compressed to an ellipsoidal shape. This first concrete indication of plastic deformation of the silica supports previous explanations of the increase in tensile strength of silica with temperature in terms of an expected plasticity.

The performance of the ring testing system at temperatures to 2200°F was most satisfactory in all respects. No difficulty was encountered with handling the samples. The silicon carbide breaking platens functioned well and showed no evidence of deterioration. The only modification of the system being considered is the substitution for or supplementation of the SR-4 pressure cell with a SR-4 load cell on which the hydraulic loading cylinder would rest. This would eliminate the necessity for extensive calibration for each series of runs.

Following completion of the capsule for the proposed high temperature irradiation of the silica, consideration was given to the sample design. Since the insulation required for the irradiation will be in the form of a ring, an obvious possibility exists for using small slip cast silica rings

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as insulators. The advantage of this approach would be that the insulating rings could be tensile tested following the irradiation, thereby markedly increasing the information yield of the experiment. Studies were begun to determine the accuracy of the ring test as applied to rings of the size required for the irradiation.

The optical hot stage was assembled and test runs were begun at elevated temperatures using both unfired and fired slip cast fused silica. As was expected, some difficulty was encountered with obtaining sufficient contrast in the silica to permit adequate definition of the particle structure. Attempts were begun to increase the viewing clarity.

First efforts were made to observe the slip casting process in alumina using motion photomicrography. Difficulties with viewing conditions, similar to those first encountered with the silica, prevented a comparison with the silica system. Work was started to improve the resolution with alumina.

A report of the progress in Phase IV will be made later in a classified supplement.

## II. Future Work

Elevated temperature tensile testing of the silica will be continued.

Tests of the silica rings for insulation of the irradiation capsule will be completed.

Alumina slips will be studied further using motion photomicrography.

Respectfully submitted,

✓ J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

September 22, 1960

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Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 22, Project No. B-153  
Covering the Period from 15 August to 15 September 1960  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

The ring tensile tester was dismantled for inspection of the breaking fixtures. Only a small crack in the silicon carbide top plate was noted. A new loading piston assembly, which should be more free from binding, was built and installed.

A series of 15 silica rings, of 9/16-inch ID and 1.5-inches OD, suitable for insulation in the high temperature irradiation experiment, was cast and fired at 2200°F for four hours. The rings were tensile tested to determine reproducibility in this smaller size. The average deviation was 17.2 per cent. A second series of 15 rings was cast of the same size but with six 3/32-inch holes arranged on 11/32-inch centers through the rings. These rings would be the configuration necessary to pass thermocouples into the monitored samples in the capsule. Following firing of the rings at 2200°F for four hours, they were tensile tested. The average deviation was 24.8 per cent when the rings were broken with no attempt being made to orient the rings in a reproducible manner during testing.

Soaking studies were begun using Ethyl Silicate 40 to decrease the porosity of the slip cast silica. A series of 3/4-inch diameter transverse bars was cast and fired for times of two, four and eight hours at 2200°F. Bars were vacuum-pressure soaked with the silicate solution and refired at 1200 and 1800°F for 16 hours. Room temperature transverse tests were made on the bars. With the 2000°F firings, the transverse strengths were uniformly increased by soaking with the 1800°F refiring giving the highest strengths. With the 2200°F firings, lower strengths were obtained after refiring the soaked bars, with the 1800°F refiring giving the lowest strengths. Although

September 22, 1960

this trend is almost certainly caused by the extent of devitrification in the silica, final analysis of the results is being delayed until the cristobalite analyses are completed.

A series of discs were prepared for determination of the influence of ethyl silicate soaking on the permeability of the silica. Initial firings and soaking were completed and refiring was begun.

An air displacement porosity system was constructed for more accurate determination of the density of alumina and silica casting. This system will also permit measurements to be made on unfired castings as well as fired.

Motion photomicrography of the silica and alumina slips was continued. Satisfactory resolution and clarity were obtained with both slips at a direct magnification of 300X. In both cases, attempts were made to follow the slip casting as the particles were drawn to a dried surface of the slip. This procedure gave quite satisfactory results with the silica but poor results with the alumina, presumably as a result of differences in drying of the two systems. Efforts were begun to form plaster sheets suitable for casting of the two slips during observation.

## II. Future Work

Elevated temperature testing of the silica will be resumed.

Initial observations will be made of the drying behavior of both silica and alumina slips.

Permeability measurements will be begun with the ethyl silicate soaked silica.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

January 23, 1961

7

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 26, Project No. B-153  
Covering the Period from 15 December to 15 January 1961  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Reinstallation of the project test systems was completed and the normal study program was resumed.

The vacuum DTA furnace was tested up to 2000°F at a pressure of approximately 1 mm. Performance of the furnace and sight port was quite satisfactory. No problem was encountered with cooling of the sight port. The vacuum maintained was sufficient to prevent oxidation of the uranium dioxide and crumbling of the pellet. Several test runs were made in vacuum with aluminum-uranium di- and octoxide pellets. Ignition of the octoxide pellets occurred at  $1600 \pm 50^\circ\text{F}$ . No crumbling of the pellets was noted before, during, or after firing. Pellets formulated using uranium dioxide failed to ignite during heating to 2000°F. In both types of pellets, some sweating of aluminum was noticed as the temperature passed the melting point of aluminum. Attempts were begun to prepare cross sections of the pellets for metallographic examination for segregation as a result of the aluminum sweating.

During the testing of the aluminum-uranium octoxide thermets, downdrive on the sample temperature axis of the recording was obtained. This apparently resulted from inability of the recorder to separate the inputs from the temperature and differential temperature connections. Runs with recordings made of the sample and unknown temperatures confirmed this observation. Modification of the x-y recorder was begun to eliminate this downdrive.

January 23, 1961

Firing of the silica tensile test rings in silicon carbide was continued. Major efforts were directed toward optimization of mold design to improve casting reproducibility. A two piece mold was developed for future production of rings. Statistical analysis was begun of the strengths of the silica cast in the two types of mold.

The arc fusion furnace was tested for production of fused silica of controlled purity. By proper control of the bleeder gate, the level of quartz in the furnace was maintained just below the arc as more quartz was added through the top of the furnace. In this fashion, a pool of fused silica was formed which grew as the unfused quartz beneath it was withdrawn from the furnace. Two pound melts of silica were produced, cleaned, and analyzed for crystallinity. X-ray traces on the fused mass showed a completely amorphous structure. Spectroscopic samples were prepared for purity analysis.

X-ray studies of the devitrification of the fused silica were continued. Runs made at 2200°F showed some signs of an induction period of a few minutes preceding formation of cristobalite. Lower temperature runs were begun to expand the induction period and improve chances of its detection.

Checks were made of the preferred cristobalite orientation previously reported for dense fused silica. Both fused silica glass and slip cast fused silica were examined. Preferred orientation was noted with the glass but not with the slip cast silica. Studies were begun to detect the influence of prior thermal history on the preferred orientation.

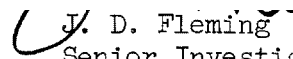
## II. Future Work

Pressing studies of the aluminum-uranium octoxide thermets will be begun. Optimum fabrication conditions will be determined.


Preliminary studies will be made of the influence of particle size on ignition point and energy yield of the thermets.

Silicon carbide firing studies will be continued using both ring tensile and transverse specimens.

Respectfully submitted,

 J. D. Fleming  
Senior Investigator

Approved:

 J. D. Walton, Head  
Ceramics Branch

**GEORGIA INSTITUTE OF TECHNOLOGY**  
**ENGINEERING EXPERIMENT STATION**  
**ATLANTA 13, GEORGIA**

23 February 1961

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 27, Project B-153  
Covering the Period from 15 January to 15 February 1961  
Contract No. AT-(40-1)-2483

Gentlemen:

I. Experimental Progress

A Tinius-Olsen Super L tensile tester was installed. Preparations were made to use this equipment for more accurate determination of the configuration constant of slip cast fused silica necessary for ring tensile testing. In order to check the accuracy of the system, a rough measurement of the Young's modulus of slip cast fused silica was made. The value of  $170 \times 10^6$  agreed well with the literature.

Statistical analysis of the two molds for casting silica rings was completed. The four piece mold previously used gave a variance in breaking load of 6100 compared with 1753 for the new two piece mold. The variance ratio of 3.46 showed high significance at greater than 1 per cent level of confidence. As a result of its demonstrated superiority, the two piece mold was chosen for all future casting work.

In-scope tests were begun of the electron microscope hot stage. Some difficulty was noted with static charge build-up on the teflon insulator on the interior of the sample holder. Modification was begun to eliminate the exposed teflon.

Preparation was begun to allow microcinematography of a whiteware slip during casting. Comparisons will be made with previous studies of alumina and silica slips.

Studies were begun to lead to microscopic examination of a thermet during firing. The characteristics of the Unitron hot stage were investigated by observing interdiffusion of carbon and tungsten thin films.

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Boundary displacement was clearly visible at temperatures in the range of the thermet firing points. In some runs, under a small partial pressure of oxygen, oxidation of the tungsten and carbon films was observed. In all cases, the image clarity was excellent.

Attempts were begun to machine graphite cups and to plasma-spray tungsten cups to contain the thermets and prevent damage of the hot stage during firing. Pellets were fired in graphite cups in the vacuum DTA furnace. Tentative results indicated that the graphite cups could contain the thermets well enough to prevent melting the hot stage. More extensive studies will be made prior to firing the thermet in the microscope.

Separation of the  $UO_2$  and  $U_3O_8$  into particle size fractions was begun. Short milling times were used in dry milling in rubber-lined mills with alumina balls to break the agglomerates. Wet screening of the milled powders was begun using acetone as the vehicle.

Oxidation rate determinations were begun for the uranium oxide powders on hand. Five gram samples were run in an air furnace using the recording balance to follow weight changes. Final weights were determined on an analytical balance following cooling of the sample. Recorded weights and analytical balance weights agreed within 5 mg. Roasting studies were begun to obtain oxides of various stoichiometry for use in the thermet investigations.

## II. Future Work

Pressing studies of thermets will be continued.

Microcinematography will be applied to the study of casting of a whiteware slip.

Stress constant determinations of the silica will be continued.

Hot stage microscopy will be continued toward inscope firing of thermets.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch



# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

March 21, 1961

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Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 28, Project No. B-153  
Covering the Period from 15 February to 15 March 1961  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Microscopic observations were made of a whiteware slip during casting. The casting behavior was very similar to that of the fused silica slip in that particle motion was highly directional and cast areas displayed little thixotropic character. This behavior is decidedly unlike that of the alumina slips previously investigated. The drying mechanism of the whiteware slip was intermediate between the alumina and silica slips. In the alumina slip, essentially no indication of drying was noted. With the whiteware slip, drying produced areas which gradually darkened, presumably through water loss. The silica, however, displayed drying areas which suddenly became opaque, perhaps through rapid water film rupture. The nature of the transformation from wet to dry in a transforming area of the silica was very reminiscent of martensitic transformations in steel, both as to speed and general appearance. Microcinematography of the whiteware slip was begun.

An apparatus was constructed in which the length and weight changes in a slip cast bar could be continuously monitored during drying. Length changes were indicated by a dial gage and weight changes were measured on an automatic electronic balance. A trial run was made using a slip cast silica bar 1/4-inch in diameter and four inches long. The bar was removed from the mold as soon after casting as possible and clamped in the test rig within two minutes. The results were somewhat surprising, showing an initial shrinkage of 0.0031 inch in a period of six minutes following the start of the test, at which time the weight loss was 0.055 gm. Following this initial contraction, the bar expanded with increasing weight loss,

regaining its original length after a period of 86 minutes at which time the weight loss was 0.495 gm. Since this weight loss was the limit of the change capacity of the balance, the run was terminated prior to the point of complete drying. The drying rate was quite low at this point. Repeat runs were begun to further explore this unexpected behavior.

In view of the poor aging characteristics of the alumina slips prepared by wet milling, attempts were begun to prepare slips from dry milled powders. Three powders were prepared by dry milling Norton 60 mesh No. 38 Alundum. The milling times for the three powders were 92, 115, and 138 hours. Eight slips were prepared from each powder using different amounts of hydrochloric acid as the peptizer. Studies were begun to determine the casting time, pH, green density, green modulus of rupture, and drying shrinkage of bars cast from the slips. The results are expected to show a correlation between the pH, or hydrochloric acid addition, and the casting characteristics, with the highest casting time, dried density, and dried strength corresponding to particular pH. The pH at which these parameters reach a maximum should be approximately 4, the pH of maximum zeta potential in alumina dispersions.

Testing was begun of a substrate heater to be used with the evaporator in producing thin films for use in the electron microscope hot state. Prototypes were operated successfully at 1700° F in vacuo. Construction of ports was begun to permit introduction of power leads to the sample chamber of the electron microscope and hot stage prototype. Some delay in the work with the microscope has been experienced as a result of its heavy use for other projects. In addition, the microscope downtime associated with installation of the hot stage has limited progress. These delays are expected to be eliminated within a few weeks by the installation of a rented RCA EMU-3 microscope which should be available for full time use by this project as required.

Modification of the x-y recorder helped but failed to eliminate the downdrive associated with DTA firings of the thermets reported in Monthly Letter Report No. 26. A number of runs were made with the uranium octoxide-aluminum thermets in which simultaneous recordings were made of the control, sample, and unknown thermocouples. Simulations of various control and measurement malfunctions narrowed the source of the downdrive to several areas of stray AC and DC pickup in the sheathed thermocouples and thermocouple leads. These pickup points were eliminated by grounding the furnace chassis, the neutral power leg at the furnace, and the thermocouple sheaths and by using shielding, grounded at the furnace and at the control panel, around the thermocouple leads.

DTA runs were begun in the air and vacuum furnaces using stoichiometric pellets of Alcoa No. 140 aluminum and the +200 cuts of fused uranium di- and octoxide. In the limited runs made to date with the octoxide pellets, a broad exothermic peak of approximately 0.5 mv occurred at 1780° F on

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vacuum firing. With air firing, the same pellets produced a sharp exothermic peak of better than 4 mv at approximately 1690° F. The first obvious interpretation for this behavior was that the aluminum oxidized rapidly in the air run or that the octoxide was reduced by the aluminum and then instantaneously reoxidized. Either mechanism would explain the sharp exothermic peak obtained in the air runs but not in the vacuum runs.

In order to explore the two possibilities suggested, two thermogravimetric runs were made in air at 30°/minute. If either of the suggested explanations applied, a rapid and appreciable weight gain should have been noted during the duration of firing which was a maximum of two minutes. In the TGA runs, a weight loss was noted at approximately 200° F, corresponding to drying of the pellet, and a weight gain was noted at approximately the firing point. The weight gain at the firing point was very slow, however, approximating a parabolic oxidation curve. The duration of the oxidation was 17.5 minutes and 20 minutes for the two runs. This order of magnitude difference in firing and oxidation times at least indicated that the sharpness of the air firing peak was due to some mechanism other than simple oxidation of the aluminum or the reduction products. The weight gain in both cases was less than that which would have been associated with complete oxidation of the aluminum by a factor of two. X-ray analysis of the products of the DTA and TGA tests was begun.

Work was begun in sealing the slip cast silica by flame glazing in an arc plasma torch and by the formulation of glazes in the low expansion system of lithium oxide, aluminum oxide, and silica.

## II. Future Work

Microcinematography will be carried out with the whiteware slip.

Further studies will be made using the length-weight change system.

Properties of the alumina slips will be determined.

Following installation of the RCA microscope, heating tests of the hot stage will be begun.

DTA and TGA investigations of the uranium octoxide-aluminum thermets will be continued.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

24 April 1961

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Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 29, Project B-153  
Covering the Period from 15 March to 15 April 1961  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Repeat runs were made in which length and weight changes were recorded during drying of a slip cast bar. In some runs, the initial shrinkage and subsequent expansion were noted as in the first tests. In other runs, however, a normal shrinkage was seen throughout. The small 1/4-inch bars used showed some signs of warping during drying under the pressure exerted by the dial gage spring. Larger bars could not be used because their weight caused overloading of the electronic balance. In order to obtain data from the larger bars, runs were begun in which shrinkage and weight loss are measured separately. In the shrinkage runs, both axial and radial dimensional changes are determined. Both 1/2- and 3/4-inch bars are being studied.

Casting times, green densities, and green strengths were determined for the alumina slips described in Monthly Letter Report No. 28. As was expected, the highest casting time and green density corresponded to a pH of approximately 4 for all particle sizes. The green densities ranged from a minimum of 64 per cent of theoretical at a pH of 4.6 to a maximum of 72 per cent at a pH of approximately 4.0. The maximum green density was the same for all three dry powders used to make the slips although their mean particle sizes varied from 11.5 to 8.5 microns. The green strengths of the slips also reached a maximum at a pH of about 4, ranging from 730 to 950 psi and decreasing with decreasing particle size. In all slips, an unexpected second maximum occurred in the green strength curves at a pH of approximately 3.7. At this pH, the dried strengths ranged from 1100 to 1300 psi. An explanation for this dual behavior is not obvious.

Sealing studies were continued in which the plasma torch was used to glaze the surface of the slip cast fused silica. Annealing of the silica prior to and following the glazing produced a crack-free glassy film. X-ray analysis was begun to detect any devitrification resulting from the glazing.

Thermal expansion tests were begun in the lithium oxide-alumina-silica system to indicate suitable combinations for glazing the silica, either by conventional techniques or by flame spraying. Samples were prepared by pressing and sintering at  $2200^{\circ}\text{F}$ , to correspond to the silica firing range, and by flame spraying.

DTA runs were continued using rough particle size cuts of  $\text{U}_3\text{O}_8$  with aluminum. Pellets were made with +150 mesh, -150 +270, and -270  $\text{U}_3\text{O}_8$  and Alcoa 140 flake aluminum. Runs were made at  $30^{\circ}\text{F}$  per minute under approximately 20 microns of air. The +150 pellets gave a broad exothermic peak of approximately 0.5 mv at about  $1830^{\circ}\text{F}$ . The pellets cracked during firing. In some runs, two other pellets were fired in silica cups at the same time as the DTA test pellet. The pellets run in the cups did not crack. In the runs with -150 +270 and -270 cuts of  $\text{U}_3\text{O}_8$ , the DTA pellet was fired in a silica cup, open at the top. These pellets did not crack during firing. The peaks obtained in these runs were sharply exothermic and occurred at  $1820^{\circ}\text{F}$  with the -150 +270 cut and at  $1730^{\circ}\text{F}$  with the -270 cut. In most cases, the platinum-rhodium thermocouple and alumina insulation were fused down, preventing an accurate evaluation of the peak height. In one run, however, the thermocouple survived and an exothermic peak height of 6.4 mv was read. Runs were begun with the +150 cut in silica cups to determine the influence of the cup.

A furnace was modified to permit simultaneous DTA and TGA runs in air. Runs were made using both unfired and fired Al- $\text{U}_3\text{O}_8$  pellets. With the fired pellets, an increase in weight started at approximately  $700^{\circ}\text{F}$  at which point the DTA showed an exothermic peak indicating  $\text{UO}_2$  oxidation. With the unfired pellets the weight change started at approximately  $1700^{\circ}\text{F}$  when the pellet fired.

X-ray diffraction examinations were made of the vacuum fired pellets from the -150 +270 cut. The traces showed predominance of  $\text{UO}_2$  with no  $\text{Al}_2\text{O}_3$  lines, presumably as a result of its smaller scattering coefficient. Little  $\text{U}_3\text{O}_8$  was observed. 18 unidentified weak lines were seen. Approximately 10 of these lines could be due to  $\text{UAl}_2$  and  $\text{UAl}_3$ .

One partially successful run was made in which an Al- $\text{U}_3\text{O}_8$  thermet was fired in the Unitron hot stage. Pictures were made successfully up to the firing point of the thermet. The shutter was open when the thermet fired,

resulting in vapor coating of the window with aluminum. Vision was thus obscured during the firing process. Damage to the hot stage was slight, consisting only of a small amount of fusion of the alumina furnace core where it touched the pellet.

## II. Future Work


Length and weight changes during drying will be measured using the larger bars.

Testing will be completed of the air balance porosity meter.


DTA and TGA tests will be continued in the Al-U<sub>3</sub>O<sub>8</sub> thermet system.

Hot stage runs with the thermets will be continued.

Respectfully submitted,

 J. D. Fleming  
Senior Investigator

Approved:

 J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

May 24, 1961

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 30, Project No. B-153  
Covering the Period from 15 April to 15 May 1961  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Trial runs were completed on the air displacement porosity meter. Using 3/4-inch silica bars fired at 1500° F for two hours, determinations were made of the apparent porosity, the bulk volume, and the apparent theoretical density. Similar determinations were made using the water displacement method in order to permit comparisons of the data. For each of the 20 specimens, three runs were made using each method, two runs by one technician and one by another. The average results of these tests are shown in Table I.

TABLE I  
EVALUATION OF AIR BALANCE\*

	<u>Air Displacement</u>		<u>Water Displacement</u>	
	<u>Tech A</u>	<u>Tech B</u>	<u>Tech A</u>	<u>Tech B</u>
% Porosity	16.35	16.34	14.05	13.60
Bulk Volume (cc)	43.34	43.32	43.36	43.27
Void Volume (cc)	7.09	7.08	6.09	5.88
Theoretical Density	2.236	2.235	2.175	2.167
Time to Run 20 Samples (min.)	105		240	

\* All results shown are averages of two runs by Tech. A and one by Tech. B on 20 samples.

A statistical analysis was made of the data. In general, this analysis indicated, within greater than the 99.9 per cent confidence level, that the air balance determinations showed no systematic differences between the results of Technicians A and B while significant differences were noted with the water displacement method. As would be expected, the porosities determined from the air balance were higher than those from water displacement. The reproducibility was better for the air balance in the void volume determinations but was essentially the same as for the water displacement method in the bulk volume determinations.

Several advantages are apparent for the air balance method. Materials can be tested which are not amenable to immersion in a liquid. This would permit testing of unfired ceramic compacts and castings. Powder samples could be used. The system is direct reading and should be suitable for automation. Samples with micropores can be tested accurately. The time required is shorter for the air balance, especially if only a few samples are to be evaluated.

A survey of the literature failed to uncover a reference to a system similar to the air balance. In view of the many advantages of the air balance system, a detailed patent search is recommended. A complete report is being prepared on the air balance for submission in case patent action is desired.

Thermal expansion tests were continued in the lithium oxide-alumina-silica system to indicate suitable compositions for use as a silica glaze. Samples were sprayed onto removable mandrels using the Metco Thermospray system.

Metallographic examinations were made of the Al-U<sub>3</sub>O<sub>8</sub> thermet pellets fired in silica cups in the DTA furnace. Relief polishing proved simple and satisfactorily outlined the microstructure. The structure of the thermet appeared to consist of a rather brittle ceramic matrix filled with relatively well dispersed particles having a metallic appearance. The particles themselves showed a duplex structure with veins of a white phase being surrounded by a more abundant gray phase. Etching of the metallic particles has not yet been attempted.

Microhardness tests were made on the particles in the thermets. A Tukon tester was used with a Knoop indenter and a 10 gram load. The hardness of the white areas ranged from 500 to 1000 with an average of 770. The hardness of the gray areas ranged from 800 to 1300 with an average of 1080. These results indicated concretely that the particles were not residual aluminum. Further identification has not yet been made.

Several successful thermet runs were made in the Unitron hot stage. Fogging of the window was eliminated by backfilling the stage with argon to a pressure of 2 psig following evacuation. Some evidence was seen of an initial reaction at approximately 1300° F although the reaction was not at all vigorous. As a result of the great thermal gradient in the furnace, the viewed surface was only at a temperature of 1500° F when the upper surface reached the ignition temperature. This prevented effective still photography of the reaction itself.



May 24, 1961

In order to explore the problems of cinematography of the reacting thermet, a series of runs was made in the hot stage in which the light level was recorded. The thermet was placed in the stage under 2 psig of argon and heated with the stage shutter open. The light emitted by the thermet was directed through the optical train of the microscope to a Photovolt photometer. The output of the photometer was fed to the X axis of a Moseley 2-S recorder. The temperature of the viewed sample surface was recorded on the Y axis of the recorder. The emitted light from the thermet peaked, during firing, at a value 1,200 times the intensity of the reflected light normally used in photography with the microscope. This indicated that a variable density filter must be used in conjunction with a strong light source if cinematography of thermet reaction is to be accomplished.

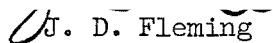
## II. Future Work

Length and weight change determinations will be continued during drying of slip cast fused silica.

DTA and TGA test will be continued in the Al-U<sub>3</sub>O<sub>8</sub> thermet system.

Cinematography of the thermet reaction will be attempted in the Unitron hot stage.

Respectfully submitted,

 J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

26 June 1961

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 31, Project No. B-153  
Covering the Period from 15 May to 15 June 1961  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Casting of molds and samples was begun for the last extensive series of studies involving slip cast fused silica. This series of tests will carry to completion the comparison of ring and conventional tensile tests and the determination of the high temperature strength of slip cast fused silica. The tests will be sufficiently large to permit statistical analysis.

Soaking studies with ethyl silicate were resumed. A series of 3/4-inch diameter silica bars was cast. Using the new air displacement porosity method, porosities of the individual bars will be determined prior to and following the initial firing and at each point in the ethyl silicate soaking process. A set of 10 bars will be used for modulus of rupture determination following each soaking so that both porosity and strength can be followed through four repeated soakings.

Microcinematography was resumed with whiteware casting slips to allow comparison with the silica and alumina casting slips. Studies of the silica and alumina casting behavior will be repeated using the improved system. Following completion of the photography, motion analysis of the casting particles will be begun.

Construction was begun of a second air displacement porosity meter to be used in the determination of the porosities of fired and unfired thermets. Analysis of the system indicated that an accuracy of better than 99 per cent is to be expected.

## REVIEW

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During the more energetic DTA firings recently carried out under vacuum, blue arcs were observed through the furnace window, running between the furnace coils and the thermet pellet. At the instant of arcing, the recorder pen was driven downscale. In addition, in a few runs, the pellet lifted off the thermocouple post during firing. In one run, the pellet struck the silica foam insulation at the top of the furnace with sufficient force to become imbedded. This behavior was apparently due to extremely rapid aluminum volatilization at the high temperatures produced during ignition. The testing procedure was modified so that the vacuum furnace was back-filled with argon to a final pressure of approximately 2 psig prior to beginning the run. The arcing and pellet movement were completely eliminated by this change in procedure.

For the first time, some DTA pellets showed signs of extensive melting during firing. The tops and sides of several pellets showed flow lines and appeared to undergo significant shrinkage. In these runs, the differential during firing exceeded 20 mv, indicating that the temperatures exceeded  $4500^{\circ}\text{F}$ . The surface temperature of the pellet was monitored with micro-optical pyrometer during some runs and was seen to exceed  $3600^{\circ}\text{F}$ . In a number of runs, the Inconel clad, magnesia insulated thermocouple was fused.

Since the loss of thermocouples was becoming quite frequent, the DTA procedure was modified in that the thermet pellet was held on an alumina spaghetti spacer rather than being in direct contact with the thermocouple. A series of tests was run using identical Al- $\text{U}_3\text{O}_8$  pellets in which four pellets were run on the alumina spacers and four were run in direct contact with the thermocouple. These runs indicated that the same ignition temperature would be determined from the test whether or not an alumina spacer was used. The peak height from the tests in which a spacer was used was approximately 25 per cent of the peak height determined with the pellet in direct contact with the thermocouple.

Confirmatory investigations were begun of the influence of  $\text{U}_3\text{O}_8$  particle size on the ignition temperature and DTA peak height. These investigations were made using more narrow particle size distributions than before, with screen cuts being made at 100, 140, 200, 270, and 325 mesh. The results of the tests obtained to date confirm the previous conclusions of a decrease in ignition temperature with particle size, consistent with increasing chemical activity accompanying the increased surface area.

## II. Future Work

Final tests of the slip cast fused silica will be continued.

The study of the influence of the  $\text{U}_3\text{O}_8$  particle size on thermet firing characteristics will be completed.

A complete study will be made of the effect of heating rate on the behavior of Al- $\text{U}_3\text{O}_8$  thermetts.

The air displacement porosity system for thermet porosity measurement will be completed.

Microcinematography of alumina, silica, and whiteware slips will be continued.

Respectfully submitted,

J. D. Fleming      ✓  
Senior Investigator

Approved:

/ J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

July 24, 1961

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 32, Project No. B-153  
Covering the Period from 15 June to 15 July 1961  
Contract No. AT-(40-1)-2483

Gentlemen:

Determinations were begun, using the air displacement system, of the porosities of the 3/4-inch diameter silica bars cast for the final firing studies. The results for four sets of bars are summarized in Table I.

TABLE I

POROSITIES OF SILICA BARS AS A FUNCTION OF FIRING CONDITIONS

<u>Firing Temperature</u> (°F)	<u>Firing Time</u> (hr)	<u>No. of Specimens</u>	<u>Average Porosity</u> (%)	<u>Apparent Theoretical Density</u> (gm/cc)
2000	4	11	16.96	2.247
2100	4	12	16.22	2.245
2200	4	11	14.34	2.246
2200*	4	12	14.38	2.246

\* Repeat run

July 24, 1961

The constancy of apparent theoretical density with decreasing porosity indicates that the firing process results in little closed pore formation. The close approach of the theoretical density to that of fused silica implies an essentially complete absence of closed porosity.

The operation of the air displacement system continued to be trouble free. The average time required to run the tests in Table I was 6.2 minutes per sample, including calculation time.

Investigations were continued of the influence of ethyl silicate soaking on the density of the slip cast fused silica. One soaking, followed by drying and firing, resulted in a decrease from an average porosity of 16 per cent to an average porosity of 13 per cent. Transverse strength determinations were begun to detect differences in strength resulting from the soaking procedure.

Microcinematography was continued with the whiteware slip and silica slip. Using transmitted light, excellent photographs were obtained of the whiteware slip. The casting and drying behavior of the slip was quite similar to that of the silica slip. The major difference noted was a tendency for the whiteware slip to dry in smaller unit areas than the silica. The photographs of the whiteware casting process showed the particle motion to be as highly directional as with the silica slip. The cast areas displayed no thixotropy.

Studies were completed of the influence of  $U_3O_8$  particle size on the ignition characteristics of Al- $U_3O_8$  thermets. The ignition temperature decreased uniformly from  $1950^\circ$  F for +100 mesh  $U_3O_8$  to  $1785^\circ$  F for -325 mesh  $U_3O_8$ . The peak height and peak area from the DTA curve failed to increase uniformly with decreasing particle size as was expected. Instead, the peak height increased from 1.48 mv for -100 +140 mesh  $U_3O_8$  to a maximum of 2.96 mv for the -200 +270 mesh cut and decreased to 1.16 mv for the -325 mesh cut. Peak areas followed the same trend, going from 93 mv-sec for -100 +140 mesh to 181 for -200 +270 mesh and decreasing to 118 for -325 mesh  $U_3O_8$ . This unexpected behavior was felt to be more the result of poor mixing than typical of the system. Attempts were begun to improve the mixing characteristics of the finer powders by vacuum drying prior to blending.

## II. Future Work

Strength determinations at elevated temperatures will be resumed with slip cast fused silica.


Check runs will be begun with the air displacement porosity system constructed for use with the thermet pellets.


Microcinematography of the alumina, silica, and whiteware slips will be continued.

Mixing studies will be begun in the Al- $U_3O_8$  thermet system.

Respectfully submitted,

Approved:

 J. D. Walton, Jr., Head  
Ceramics Branch

 J. D. Fleming  
Senior Investigator

**GEORGIA INSTITUTE OF TECHNOLOGY**  
**ENGINEERING EXPERIMENT STATION**  
**ATLANTA 13, GEORGIA**

August 25, 1961

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 33, Project No. B-153  
Covering the Period from 15 July to 15 August 1961  
Contract No. AT-(40-1)-2483

Gentlemen:

A three factor variance analysis was made of the factors influencing the ring tensile test. The factor showing the greatest influence was a lack of adequate reproducibility of the firing conditions. This factor and the second order interactions in which it appeared were strongly significant at greater than the 95 per cent level of confidence. Sample to sample variations within a given firing and use of different testing machines showed little influence on the average test results.

The first series of runs was completed in the determination of the tensile strength firing profile for slip cast fused silica. The results of this series of brittle ring tensile tests showed that the relationship between tensile strength and firing conditions is quite similar to that between the modulus of rupture and firing conditions. The tensile strengths were slightly, but not significantly, lower than the corresponding moduli of rupture. The maximum room temperature tensile strength was 4300 psi, reached after firing one hour at 2300° F.

Investigations were completed in the high temperature x-ray diffraction unit to compare the devitrification rates of silica castings from different mold plasters. These tests showed that the surface devitrification rate is highest if the casting is fired with Keltex mold release in place. In decreasing order of surface devitrification rate, the other conditions ranked:

1. Casting without a mold release.
2. Casting with either U. S. Gypsum No. 1 or Bestwall K-59 plaster.
3. Casting with U. S. Gypsum Puritan plaster.

August 25, 1961

The devitrification rates varied qualitatively in proportion to the surface calcium content as determined by x-ray fluorescence.

Tests were begun to survey the possibility of determining firing profiles from bars fired in gradient furnaces. Sections are being cut from bars fired at 2000, 2100, and 2200° F for 2, 4, 8, and 16 hours and at 2300° F for 1/2, 1, 2, and 4 hours. The crushing strengths of these bars will be determined and used to plot firing profiles for comparison with modulus of rupture and tensile strength profiles. If the shapes of the curves are similar crushing tests will be begun using isothermal sections cut from bars fired in gradient furnaces.

Approval was received for operation of the krypton tracer permeation system with direct release of the krypton to the atmosphere. This modified permeation system will permit much faster tests since one replotting of the raw data will yield values for the effective diffusivity. After construction of the hood required for the new system, studies will be begun to evaluate the effectiveness of sealing the slip cast fused silica by flame glazing with an arc-plasma torch.

Experiments were made to determine the influence of excess reactants on the ignition characteristics of aluminum-U<sub>3</sub>O<sub>8</sub> thermetts. Both excess aluminum and excess U<sub>3</sub>O<sub>8</sub> produced more vigorous reactions. While this was expected with the excess of the aluminum liquid phase, the effect of excess U<sub>3</sub>O<sub>8</sub> was surprising. The only explanation proposed so far is that the loss of reaction energy as latent heat in evaporated aluminum was decreased. Thermogravimetric studies are planned to investigate this effect further.

## II. Future Work

X-ray tests will be carried out to determine the effect of the graphite mold release on devitrification rates of cast fused silica.

Attempts will be made to produce more reproducible firings of the silica rings. Lower temperature firing will be used to bring the cristobalite formation rate within a range where it is not so critically dependent on temperature. Rings will also be separated during firing by silicon carbide spacers.

Further runs will be made in the statistical evaluation of the ring test.

Mixing studies will be continued in the Al-U<sub>3</sub>O<sub>8</sub> thermet system.

Respectfully submitted,

Approved:

J. D. Fleming  
Senior Investigator

J. D. Walton, Jr., Head  
Ceramics Branch



# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

September 25, 1961

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 34, Project No. B-153  
Covering the Period from 15 August to 15 September 1961  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Exploratory tests were made in which crushing strengths were determined for slip cast fused silica bars which had been tested for modulus of rupture. Sets of seven bars were used which were fired at 2200° F for 2, 4, 8, and 16 hours. One 3/4-in. long section was cut from each 3/4-in. diameter bar using a diamond saw. Care was taken to produce plane and parallel saw cuts. The top and bottom faces of the test specimens were cushioned with cardboard during crushing to minimize chipping. A spherical bearing block was used at one end of the specimen to accommodate lack of parallelism of the two cylinder ends. The sections were crushed at a loading rate of 2400 pounds per minute on a Tinius Olsen Super L universal tester. With the exception of the 16 hour firing, the crushing strength was approximately four times the modulus of rupture. For the 16 hour firing, the crushing strength was almost ten times the modulus of rupture. This difference was found to be due to extensive crack formation, parallel to the axis of the bar, on longer firing. The modulus of rupture test proved to be more sensitive to the cracks in view of the perpendicular load application resulting in the cracks acting as weak fibers. In the crushing test, the cracks amounted to no more than axial column formers and, since each column was loaded axially, a less severe decrease in crushing strength resulted. Although the maxima in the 2200° F firing profiles could not be located accurately with only four firing times, the modulus of rupture appeared to peak at 6 hours compared with 7 hours for the crushing strength. Plans were made for supplementary studies of the crushing test.

Brief studies were made in which slip cast fused silica was fired in an argon atmosphere. Indications were given that the strengths of the argon fired bars were significantly lower than those of air fired bars. Since oxygen is

## REVIEW

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known to accelerate devitrification in fused silica, these results would tend to indicate a devitrification dependence of strengthening in slip cast fused silica. This supports the bonding mechanism previously postulated. More extensive firings will be made in inert and devitrification-active atmosphere to provide statistically valid comparisons.

Elevated temperature tensile testing of the fused silica was temporarily suspended to allow equipment modification and possible improvement of the ring firing procedures.

Low temperature firing studies were begun with the slip cast alumina. Four hour firing at 2200° F produced moduli of rupture of approximately 13,000 psi.

X-ray analyses were completed for relative  $UAl_2$  and  $UAl_3$  content of all Al- $U_3O_8$  thermets run to date. No systematic correlation was apparent for the variation in relative  $UAl_2$  and  $UAl_3$  content with ignition temperature, peak height, or peak area. Several trends were noted, however, which will bear further study. Generally, the relative amounts of  $UAl_2$  and  $UAl_3$  are inversely related, i.e. high  $UAl_2$  content usually occurs in samples with low  $UAl_3$  content and vice versa. This is consistent with the stoichiometry of the system assuming complete reaction of all the aluminum and  $U_3O_8$  and assuming no gain or loss of material from the pellet. Under these circumstances, as the amount of  $UAl_3$  increases, the amounts of  $UAl_2$  and  $Al_2O_3$  should decrease and the amount of  $UO_2$  should increase. This reasoning would also imply an increase in energy evolution with decreasing final  $UAl_3$  content. Some indication of such a trend was obtained.

Thermets compounded from  $U_3O_8$  of a particle size in excess of 140 mesh showed incomplete reaction since residual  $U_3O_8$  was detected in the x-ray traces. A  $U_3O_8$  particle size of +100 mesh showed very little reaction as indicated by the complete absence of  $Al_2O_3$  lines from the trace. All other samples showed strong lines of  $UO_2$ ,  $UAl_2$ , and  $UAl_3$ , weak lines of  $Al_2O_3$  and no trace of  $U_3O_8$  or U. In general, the amount of  $UAl_2$  increased with decreasing particle size.

## II. Future Work

Studies of ring firing procedures will be continued.

More extensive firings of the slip cast fused silica will be made in neutral and devitrification-promoting atmospheres.

Low temperature firing of slip cast alumina will be continued.

Several Al- $U_3O_8$  thermets will be subjected to microprobe analysis.

Approved: ,

Respectfully submitted,

J. D. Walton, Head  
Ceramics Branch

J. D. Fleming  
Senior Investigator

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

October 26, 1951

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 35, Project No. B-153  
Covering the Period from 15 September to 15 October 1961  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Firing of the slip cast fused silica was continued in the low and intermediate temperature regions. Runs will eventually be made at 33° F intervals from 1800 to 2300° F. The firing times at each temperature will be extended gradually until the point of maximum strength development is well defined. In the additional runs completed at 2100, 2133, and 2166° F, indications have been obtained that the same maximum modulus of rupture is reached regardless of the firing temperature employed. These runs and those at 2200 and 2300° F previously reported (Progress Report No. 3) all showed maximum moduli of rupture of approximately 4700 psi. The time at which this maximum was reached varied significantly with firing temperature. At a firing temperature of 2300° F, the maximum strength was attained after one hour while approximately 48 hours was required at 2100° F. These results proved graphically the strong influence of temperature on firing properties and supported long time, low temperature firing as a means of minimizing the effects of furnace temperature gradients, particularly with large shapes.

Using the air displacement technique, measurements were made of porosity, theoretical density, and bulk density for the 2100, 2133, and 2166° F firings. As before, bulk and theoretical densities increased continuously with increasingly severe firing conditions. The porosity showed an initial decrease on more severe firing, reached a minimum under firing conditions corresponding to the point of maximum strengthening, and increased with further firing.

Devitrification rate studies were made in the high temperature x-ray diffraction system using samples cast into U. S. Gypsum No. 1 plaster with the graphite mold release. Graphite proved as effective as Keltex in restricting

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impurity leaching from the plaster. The devitrification rate with the graphite release was low even though the specimens were fired without having the graphite removed. Mold contaminants held on the surface of the graphite were apparently removed by burning off the graphite and did not become fixed by the silica. An ammonium alginate was ordered for similar testing. Provided this material is sufficiently free of alkali contaminants, samples cast using this release can probably be fired without prior film removal as was found necessary with Keltex.

Construction of the modified krypton permeation system was completed. Performance tests of the sample chamber will be carried out in the near future and permeation studies will be made using the flame glazed silica discs.

Further attempts were begun to identify the phases produced in the Al-U<sub>3</sub>O<sub>8</sub> thermet reaction. Several samples were etched for 24 hours in 1N sodium hydroxide solution at room temperature to remove residual aluminum. Most of the samples were completely unaffected by this solution. Following this treatment, the samples were immersed in 1N sulfuric acid at room temperature. All samples showed pitting in the regions of metallic appearance, indicating that these areas were probably aluminum-uranium intermetallic compounds. Further immersion of the samples in 1N nitric acid produced some pitting of the grey areas, implying the presence of uranium dioxide. Spectrographic and chemical analysis of the extracts from the etching operations was begun to delineate the phases attacked.

Preparation of samples was begun for electron microscopy of the thermetts. Both extractive replication, using cellulose acetate and polyvinyl alcohol, and microtomy will be investigated. Neither of these techniques has produced definitive results to date.

Arrangements were made for thermet samples to be subjected to microprobe analysis at Advanced Metals Research, Sommerville, Mass. Representative areas will be scanned for aluminum and uranium content. Qualitative, if not quantitative, identification of the phases is expected.

## II. Future Work

Firing of the slip cast fused silica will be continued at low and intermediate temperatures to the point of maximum strengthening.

Investigations will be made of the influence of ammonium alginate mold release on surface devitrification of slip cast fused silica.

Low temperature firing of slip cast alumina will be continued.

Efforts will be extended to identify Al-U<sub>3</sub>O<sub>8</sub> thermet phases by chemical and microprobe analysis and electron microscopy.

Respectfully submitted,

Approved:

U J. D. Walton, Head  
Ceramics Branch

U J. D. Fleming  
Senior Investigator

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION  
ATLANTA 13, GEORGIA

November 27, 1961

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 36, Project No. B-153  
Covering the Period from 15 October to 15 November 1961  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Firings of slip cast fused silica were carried out in vacuum, air, steam, and argon. These firings were made to determine the changes in firing characteristics of slip cast fused silica resulting from firing in atmospheres differing in devitrification promoting ability. In the argon firings, the tube was evacuated and backfilled with argon several times prior to being filled to a positive gage pressure. As a result, the argon firings were characterized by the lowest concentration of devitrification promoting gases. The vacuum runs were next lowest in active gas content. Two hour runs at 2200° F were completed with air, argon, and vacuum. A four hour run at 2200° F was made with steam. Air displacement porosities and densities and moduli of rupture were determined. The data are summarized below. Since the data were obtained in a tube furnace without accurate knowledge of the centerline temperature, the results can only be compared internally. It is of interest, however, to note that the steam fired porosity of 10.65 per cent is substantially lower than the porosities measured under any normal firing conditions.

In view of the marked effect of firing atmosphere on the silica, further experiments were planned for more closely controlled firing conditions. X-ray analyses were begun to determine the cristobalite content of the fired bars.

## REVIEW

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TABLE I  
FIRING CHARACTERISTICS OF FUSED SILICA IN DIFFERENT ATMOSPHERES\*

<u>Atmosphere</u>	<u>Porosity</u> (%)	<u>Apparent Theoretical Density</u> (gm/cc)	<u>Bulk Density</u> (gm/cc)	<u>Modulus of Rupture</u> (psi)
Argon	17.26	2.221	1.837	460
Vacuum	16.04	2.225	1.869	1880
Air	15.81	2.228	1.876	2670
Steam	10.65	2.244	2.005	3650

\* Argon, vacuum, and air firings at 2200° F for 2 hours. Steam firing at 2200° F for 4 hours.

Check out runs were begun with the one-sided krypton permeation system. With the disc holder completely sealed, the krypton leakage rate was negligible. Three runs were made with one silica sample. The effective diffusivities were all within three per cent of the mean. Runs were begun to correlate the permeability with porosity and to evaluate the effectiveness of plasma-jet sealing of the porous slip cast silica.

Further studies were carried out in the analysis of the Al-U<sub>3</sub>O<sub>8</sub> thermets. Alpha count rate measurements were made for each of the three solvents applied to selective phase attack. The sodium hydroxide solution failed to show any alpha activity, confirming the expected attack on residual aluminum and the lack of attack on uranium-aluminum intermetallic compounds. Both the sulfuric and nitric acid solutions showed appreciable alpha activity, indicating the expected attack on uranium-aluminum intermetallics and uranium dioxide.

Representative thermet samples were prepared for electron microprobe analysis. Following metallography for phase typing, the samples will be forwarded to Advanced Metals Research for analysis.

November 27, 1961

II. Future Work

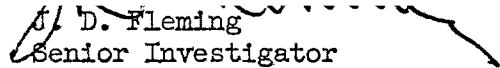
Expanded studies will be made to determine the influence of atmosphere on the firing characteristics of slip cast fused silica.

Low temperature firing of slip cast alumina and silica will be continued.


Studies will be made of casting under pressure to increase the casting rate of the alumina slip.

Further chemical analyses will be made in the Al-U<sub>3</sub>O<sub>8</sub> thermet systems.

Respectfully submitted,

  
J. D. Fleming  
Senior Investigator

Approved:

 J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

December 22, 1961

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 37, Project No. B-153  
Covering the Period from 15 November to 15 December 1961  
Contract No. AT-(40-1)-2483

Gentlemen:

Further firings of slip cast fused silica were made in argon, air, vacuum, and steam. The argon and air firings were completed, the steam firings were carried through eight hours and the vacuum firings through two hours, all at 2200° F. The porosities and moduli of rupture are summarized in Table I.

TABLE I

PROPERTIES OF SLIP CAST FUSED SILICA  
FIRED AT 2200° F IN VARIOUS ATMOSPHERES

	Firing Time (hr)			
	2	4	8	16
<u>Argon</u>				
MR (psi)	462	876	1480	1420
Porosity (%)	17.26	16.46	16.44	15.98
<u>Vacuum</u>				
MR (psi)	1640	-	-	-
Porosity (%)	16.29	-	-	-
<u>Air</u>				
MR (psi)	2670	4180	2770	2070
Porosity (%)	15.81	14.63	15.19	15.35
<u>Steam</u>				
MR (psi)	5472	3646	1523	-
Porosity (%)	11.28	10.65	10.14	-

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Although the steam firing showed a drop in modulus of rupture past a two hour firing time, no gross internal structural flaws were observed in broken samples from the longer firings. Cristobalite analyses were not completed. The physical data indicate, however, that steam is quite effective in promoting devitrification induced bulk diffusion. The data show that the rapid diffusion with steam firing might permit lower temperature firing with greatly enhanced densification.

Curves were plotted of the porosity of slip cast fused silica air fired under different conditions using the minimum porosity firing time as a normalizing factor. Under these conditions, all porosity values fell closely along a single line, reaching a minimum porosity of approximately 14.4 per cent.

Studies were made of the effects of vibration and pressure application on the casting characteristics of the alumina slip. Although the number of runs was too small to allow reliable quantitative correlation, certain qualitative observations were made. Vibration seemed effective in filling the mold and in permitting sound castings to form in adjacent thick and thin sections. Pressure application proved highly advantageous. Casting of quite complex structures was possible in unvented molds since air was easily forced through the mold pores, allowing the slip to fill the mold completely. In addition, as should be the case, casting time for a 3/4-inch bar decreased roughly linearly with an increase in the applied pressure. In the absence of pressure, the casting time was about eight hours. At 20 psig, the casting time was four hours, at 40 psig, two hours, and at 60 psig, the limit for plaster molds, 90 minutes. If silica molds could be used, the higher strength should permit application of at least 600 psi, producing a still shorter casting time.

Initial firings were made with aluminum- $U_3O_8$  pellets surrounded with magnesium oxide insulating powder. The effects of aluminum evaporation were graphically demonstrated. When the pellets were fired under a pressure of approximately 30 microns of argon, complete disintegration occurred with considerable arc-over in the aluminum vapor in the furnace. Under one atmosphere absolute of argon, the pellet remained intact although frothing was still noted and some arc-over remained. Under two atmospheres absolute of argon, very little frothing was observed and little arc-over occurred.

## II. Future Work

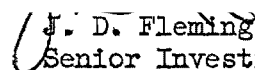
Low temperature firing of slip cast fused silica will be carried out in steam.

Porosities will be determined for alumina bars slip cast under pressure.

Further firings of the aluminum- $U_3O_8$  thermets will be carried out in magnesia insulation.

Respectfully submitted:

Approved:

 J. D. Fleming  
Senior Investigator

/ J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

January 22, 1962

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 38, Project No. B-153  
Covering the Period from 15 December 1961 to January 1, 1962  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Samples of the fused silica fired in steam, air, argon, and vacuum were prepared for x-ray analysis. Since a tube furnace was used for the firings, substantial thermal gradients occurred in the outer and inner rings of fused silica bars. The two groups showed noticeably different strengths and porosities. One sample at the porosity average will be selected from each group for initial x-ray analysis. All samples will be analyzed ultimately.

Firings were begun of slip cast fused silica rings using alumina spacers to achieve more uniform temperature distribution. These rings will be tested at room temperature in the ring tensile tester and in a Tinius Olsen universal tester. A complete analysis of variance will be carried out to evaluate the uniformity of firing.

Construction was begun of a Krypton 85 storage tank and injector to be used with the permeation system. This apparatus is necessary in order to insure compliance with operating restrictions on Kr-85 release. A gas syringe will be used to inject reproducible amounts of the tracer gas, permitting consistent operation at the highest allowable count rates.

Additional ignitions of aluminum-U<sub>3</sub>O<sub>8</sub> thermets were carried out in magnesia insulation. With the higher net energy yields resulting from the insulation, downdrive again was noted on the temperature axis during ignition. In order to eliminate this difficulty, design of a differential bridge circuit was begun. This circuit should completely isolate the temperature and differential temperature axes, making ignition interference with the temperature measurements impossible.

II. Future Work

The slip cast fused silica rings will be tested and data analysis will be begun.

The Kr-85 injector will be completed and permeability measurement will be resumed.

The DTA differential bridge will be completed and firings of aluminum- $U_3O_8$  thermets will be carried out in magnesia insulation.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

February 15, 1962

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 39, Project No. B-153  
Covering the Period from 1 January to 1 February 1962  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Firing of silica rings was resumed for completion of the determination of the tensile strength of slip cast fused silica. The rings are being fired while separated by alumina spacers. Separation of the rings should allow more uniform heat penetration and result in more reproducible sample strengths. Six firings will be made initially. Half of each firing will be broken on the ring tensile tester and half on the Tinius-Olsen universal tester. The data will be subjected to a complete statistical analysis for sample, firing, and machine differences.

The krypton-85 storage tank was completed and safety checks were begun. Following completion of these tests, permeability runs will be resumed with slip cast fused silica fired under various conditions and plasma-arc glazed.

A study was made of the influence of casting pressure and mold vibration on the casting characteristics of alumina slips. The slip was prepared by wet milling 2000 gm. of Norton 220 mesh type 38 Alundum with 411 ml. of de-ionized water and 25 ml. of concentrated hydrochloric acid. The slip was ground for 90 hours at 67 rpm in a one gallon porcelain mill. The resulting slip contained 82.1 per cent solids, had a viscosity of 2,700 cp. (Brookfield, 30 rpm spindle no. 3), and a pH of 3.9. Test bars 3/4-in. in diameter by 5-5/8-in. long were cast in one piece graphite coated plaster molds. Pressures of 20, 40, and 60 psig were applied. At each pressure, axial vibration was applied to the molds at 60 cps with a Syntron vibrating table. Vibration amplitudes were 0.01, 0.012, and 0.015-in. The bars were dried at 230° F for 24 hours prior to testing. The results of the tests are summarized in Table I.

## REVIEW

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TABLE I  
PROPERTIES OF ALUMINA BARS CAST WITH PRESSURE AND VIBRATION

<u>Mold Pressure</u> (psig)	<u>Vibration Amplitude</u> (in)	<u>Casting Time</u> (hr)	<u>Porosity</u> <sup>*</sup> (%)	<u>Bulk</u> <sup>*</sup> <u>Density</u> (gm/cc)	<u>Theoretical</u> <sup>*</sup> <u>Density</u> (gm/cc)	<u>Green Modulus of Rupture</u> (psi)
20	0.010	4.75	32.3	2.54	3.75	1700
20	0.012	5	31.4	2.57	3.75	1800
20	0.015	7	30.9	2.59	3.75	1800
40	0.010	1.75	32.9	2.52	3.75	1500
40	0.012	2	32.6	2.53	3.75	1600
40	0.015	4.5	31.2	2.58	3.75	1700
60	0.010	1.5	32.8	2.52	3.75	1600
60	0.012	1.75	32.7	2.52	3.74	1600
60	0.015	2	31.2	2.58	3.75	1700

\*Determined by air displacement

A series of mixing studies was run in which 0.1 and 1 w/o dry Baymal (DuPont colloidal alumina) was incorporated in the standard Al-U<sub>3</sub>O<sub>8</sub> thermet mixture prior to dry mixing. Pellets pressed with the Baymal mixture showed substantially greater energy yields upon ignition as well as much more uniform structures following ignition. The pellets appeared to produce more evaporation of aluminum during ignition, presumably because of the greater energy yields. Arc-over in the furnace during ignition was quite common. Attempts were begun to eliminate the arc-over.

## II. Future Work

Tensile testing of the silica will be resumed.

Following completion of the safety checks on the krypton-85 storage chamber, permeation testing will be begun.

Further studies will be made of the effects of Baymal additives on the firing characteristics of the Al-U<sub>3</sub>O<sub>8</sub> thermets.

Respectfully submitted,

Approved:

J. D. Walton, Head  
Ceramics Branch

J. D. Fleming  
Senior Investigator

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

March 13, 1962

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 40, Project No. B-153  
Covering the Period from 1 February to 1 March 1962  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Low temperature firings of slip cast silica were extended to 64 hours at 2000° F, 68 hours at 2100° F, and 24 hours at 2133° F and 2166° F. The minimum porosity firing point was not enclosed by the 2000° F firings but was for the other firings. The integral firing time apparently closest to the minimum porosity condition is given as a function of firing temperature in Table I. Since the point of minimum porosity corresponds to the maximum cristobalite formation and bulk diffusion without development of major structural flaws as a result of post-firing thermal shock, this time should approximate closely the firing time for maximum strength development. Incomplete modulus of rupture determinations tentatively support this conclusion.

TABLE I  
APPARENT FIRING TIME FOR MINIMUM POROSITY AND  
BULK DENSITY OF SLIP CAST FUSED SILICA

<u>Firing Temperature</u> (°F)	<u>Apparent Time for Minimum Porosity</u> (hr)	<u>Apparent Minimum Porosity</u> (%)	<u>Corresponding Bulk Density</u> (gm/cc)
2000	>64	>15.88	>1.884
2100	48	14.19	1.934
2133	16	14.36	1.923
2166	12	14.37	1.945
2200	4	14.38	1.922
2300	1	14.02	1.951

A series of six ring firings was made at 2200° F for four hours with the rings separated by alumina tripod separators. Six stacks of four rings each were used in each firing. Half of each firing was broken on ainius-Olsen Super L tester and half on the ring tensile tester. The tensile data are being subjected to an analysis of variance. Results obtained so far indicate that the effect of the testing machine is not significant. Effects due to different firings were not significant. Sample variations within a given level, for instance within the top rings in all stacks, were not significant. Sample variations within a given stack, however, proved to be significant. Further analysis will be made treating the levels as replicates.

Safety checks were completed with the modified Kr-85 permeation system. No difficulties were encountered. Several runs were made to determine the minimum activity to give a clearly legible permeation trace. Two cc. of the diluted Kr-85 gave a suitable trace and was adopted as the standard tracer loading for future runs. This corresponds to roughly 0.5 mc of Kr-85. Preparation of fused silica discs was begun for permeation testing.

A composition scan of the Al-U<sub>3</sub>O<sub>8</sub> thermet system was begun at increments of 10 w/o aluminum. The DTA curves might be expected to show an increase in peak height, for a given amount of U<sub>3</sub>O<sub>8</sub>, up to the point where the maximum amount of reaction is possible. Since the ignition temperatures observed so far have all exceeded the peritectic decomposition temperature of UAl<sub>4</sub>, this point would correspond to complete reduction of all the U<sub>3</sub>O<sub>8</sub> to UAl<sub>3</sub>, possible with 31.4 w/o of aluminum. With aluminum contents in excess of this amount, the aluminum in excess of 31.4 w/o should act only as a diluent and a decrease in peak height should occur with increasing aluminum. In practise, the actual composition at which the maximum peak occurs will probably be less than 31.4 w/o aluminum since complete reduction of the UO<sub>2</sub> resulting from the U<sub>3</sub>O<sub>8</sub> will probably not occur. Results obtained so far imply that this maximum peak composition is between 20 and 30 w/o aluminum.

## II. Future Work

Analysis of the ring firing and tensile testing will be continued.

Permeation testing of the slip cast fused silica will be resumed.

Further DTA tests will be made with Al-U<sub>3</sub>O<sub>8</sub> thermets of different composition.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION  
ATLANTA 13, GEORGIA

April 13, 1962

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 41, Project No. B-153  
Covering the Period from 1 March to 1 April 1962  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Work

The initial study was completed in the investigation of the effects of the firing atmosphere on the characteristics of slip cast fused silica. The influence of steam was quite remarkable in that the time required to fire to maximum strength at 2200° F was only a fourth that in air. In addition, steam appeared to increase the rate of bulk diffusion appreciably since the porosity was approximately 40 per cent lower than in air firing. Formation of internal fractures was much less prominent in the steam firing as indicated by a continued decrease in porosity even after the point of maximum strength was passed. The devitrification rate was somewhat higher with steam than with air in agreement with the literature. Firing in argon produced opposite effects. Compared with results from air firing the argon firing resulted in higher porosities, lower strengths, and lower devitrification rates.

The first series of low temperature firings was completed with the slip cast alumina. 3/4-in. diameter by 5-5/8-in. long bars were cast into one piece plaster molds coated with the graphite mold release. During casting, the molds were subjected to axial vibration at 60 cps with an amplitude of 0.015-in. and to a pressure of 60 psig. Following casting, the bars were air dried in the molds for 24 hours, dried at 130° F for 24 hours and at 330° F for 16 hours. Sets of dried bars were heated at 1000° F per hour to 2030, 2140, and 2250° F and soaked for 8 hours. After being fired, the bars were furnace cooled. The properties of the unfired and fired bars are summarized in Table I.

## REVIEW

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TABLE I  
PROPERTIES OF SLIP CAST ALUMINA

<u>Firing Temperature</u> (°F)	<u>Modulus of Rupture</u> (psi)	<u>Porosity</u> (%)	<u>Bulk Density</u> (gm/cc)	<u>Apparent Theoretical Density</u> (gm/cc)
Unfired	~ 1,700	32.7	2.576	3.83
2030	13,800	32.1	2.629	3.88
2140	15,800	29.8	2.67	3.80
2250	17,000	28.1	2.76	3.84

Several runs were made of a 59.7 w/o Al - 40.3 w/o  $U_3O_8$  thermet. These samples failed to give a sharp ignition peak but a noticeable exotherm occurred at approximately 1050° F. The DTA chart showed a pronounced endotherm at the melting point of aluminum and, in some cases, a second exotherm which began during or immediately after melting of the aluminum. The peak heights observed in the tests were quite low, indicating a low temperature excursion during firing. The reaction did not appear at all violent. X-ray diffraction analyses were made of samples heated to 1200, 1300, 1900, 2000, and 2100° F. The results were not entirely consistent in that the 1200, 1900, and 2100° F samples showed strong traces for  $UAl_4$  and  $Al_2O_3$  but no traces for residual  $U_3O_8$ ,  $UO_2$ ,  $UAl_2$  or  $UAl_3$ . Conversely, the 1300 and 2000° F samples showed no  $UAl_4$  but did show residual  $U_3O_8$  and traces for  $UO_2$ ,  $UAl_2$  and  $UAl_3$ . These results would imply that complete reaction of the  $U_3O_8$  in a 59.7 w/o Al thermet can occur as low as 1200° F, below the melting point of aluminum but more work must be done to discover the reason for the lack of reaction in some samples.

## II. Future Work

More firings of slip cast fused silica will be made in steam at lower temperatures.

Investigations will be resumed in the determination of the influence of firing conditions on the krypton permeability of slip cast fused silica.

Reactor Division  
Oak Ridge Operations Office

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April 13, 1962

Longer time firing will be carried out with slip cast alumina.

Further studies will be made with higher aluminum content Al-U<sub>3</sub>O<sub>8</sub> thermets.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION  
ATLANTA 13, GEORGIA

May 16, 1962

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 42, Project No. B-153  
Covering the Period from 1 April to 1 May 1962  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Since the slip cast fused silica is fired by being placed cold into a preheated furnace, some firing occurs during the time the furnace requires to re-heat to the firing temperature. The bulk density profile was found to plot as a straight line on semilog paper, providing a basis for extrapolation through the unfired bulk density to yield a firing correction time. Least squares fits of the bulk density data were used to locate the firing time correction which proved to be very close to the heat-up time for all firing temperatures except 2300° F. Even for the 2300° F firings, the line fit was not noticeably affected by the use of the actual heat-up time. These correction times will be applied to all firing data in the future in order to correlate unfired and fired properties on the same time scale. The firing time corrections are given in Table I.

Determinations of the modulus of rupture and porosity were completed for all firings at 2000, 2100, 2133, 2166, 2200, and 2300° F. The firing times enclosed the times for minimum porosity and maximum strength for all temperatures except 2000° F. At 2000° F, extrapolation indicated that the time for maximum strength would be about 160 hours, an impractical firing time for anything but very large shapes. The firing times for maximum strength and minimum porosity, obtained by four point Lagrangian interpolation of graphical data, are given in Table I.

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Oak Ridge Operations Office

May 16, 1962

TABLE I

FIRING TIME CORRECTIONS AND PEAK FIRING TIMES  
FOR SLIP CAST FUSED SILICA

<u>Firing Temperature</u> (°F)	<u>Firing Time Correction</u> (hr)	<u>Corrected Time For</u>	
		<u>Minimum Porosity</u> (hr)	<u>Maximum Modulus of Rupture</u> (hr)
2000	0.23	160	-
2100	0.32	46.7	49.0
2133	0.35	17.4	19.0
2166	0.37	12.4	8.5
2200	0.38	5.7	3.3
2300	0.79	2.0	1.6

The shorter corrected firing time for peak modulus of rupture than for minimum porosity indicates that post-firing cristobalite thermal fracture exerts a more pronounced effect on strength than on porosity. This behavior was expected.

Results were obtained from the electron microprobe analysis of the 14.6 w/o Al, 85.4 w/o U<sub>3</sub>O<sub>8</sub> thermets. The analyses were based on Al<sub>2</sub>O<sub>3</sub>, UAl<sub>4</sub>, and UO<sub>2</sub> standards. Analysis for UAl<sub>2</sub> was based on extrapolation of the results for UAl<sub>4</sub>. In the samples investigated, only UAl<sub>2</sub>, UO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> were detected. All areas of metallic appearance in the microstructure proved to be UAl<sub>2</sub>. Although some UAl<sub>3</sub> was detected by x-ray analysis of similar pellets, the microprobe indication of only UAl<sub>2</sub> as the metallic phase is not inconsistent. The fact that these pellets contained somewhat less aluminum than is required for complete conversion of all the uranium to UAl<sub>2</sub> would imply that only a limited amount of UAl<sub>3</sub> would be formed. Since no more than three metallic areas were scanned in any sample, it is not unlikely that the UAl<sub>3</sub> areas indicated by x-ray were simply not selected for microprobe scans.

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Oak Ridge Operations Office

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Further ignitions of 7.9 w/o Be, 92.1 w/o  $U_3O_8$  thermets were made. The ignition peaks continued to appear at about 1820° F and were somewhat larger than the peaks observed with Al- $U_3O_8$  thermets. The reactions seemed somewhat less rapid than those with Al- $U_3O_8$ . While the Al bearing pellets ignited almost instantaneously, the high temperature reaction line could be seen to move slowly in the Be bearing pellets. The reactions required several seconds to become complete.

## II. Future Work

Firing of fused silica rings for the tensile test will be resumed.

Steam firing of the silica will be continued.

Further ignitions will be made with high Al- and with Be- $U_3O_8$  thermets.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

June 15, 1962

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 43, Project No. B-153  
Covering the Period from 1 May to 1 June 1962  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Work

Statistical analysis of the ring firing data was completed. In order to maximize the information yield, first, second, and third order interactions were examined treating the stacks, rows, and rings as replicates. These studies indicated that the position of the sample in the furnace and all interactions involving this variable were significant. The principal source of sample variation thus appeared to be temperature gradients within the furnace. Since finances do not permit rebuilding the furnace, a modification in the tensile test program will be necessary. Larger sample populations will be tested at fewer firing and testing conditions. The data will be subjected to statistical analysis to evaluate quantitative trends.

An air displacement porosimeter was constructed to permit measurement of the porosity of the silica discs used in the tracer determination of permeability. Since this system was designed to handle 3/4-inch diameter bars as well as discs, a direct comparison with the original air displacement porosimeter was possible. Four replicate porosity measurements were made for a set of ten silica bars using each system. The new system indicated an average porosity of 13.96 per cent compared with 14.00 per cent for the original system. Porosity measurements and permeability testing of slip cast fused silica discs were begun. In the initial series of investigations, tests will be made with silica fired under different conditions.

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Reactor Division  
Oak Ridge Operations Office

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June 15, 1962

Studies were begun in the Al-U<sub>3</sub>O<sub>8</sub> system to determine more precisely the lowest temperature at which rapid reaction begins. A series of compacts, covering the composition range from 4.27 to 65 w/o aluminum, was fired to 1200° F at 60° F per minute. The pellets are being examined by x-ray diffraction and chemical analysis for evidence of reaction. Similar experiments will be carried out with terminal firing temperatures of 1400 and 1600° F.

## II. Future Work

Fused silica ring firings will begin for the revised tensile testing schedule.

Porosity and permeability measurements will be continued with silica discs fired under different conditions.

Low temperature firings will be continued with Al-U<sub>3</sub>O<sub>8</sub> thermets. X-ray analysis of the first series of pellets will be completed.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

July 11, 1962

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 44, Project No. B-153  
Covering the Period from 1 June to 1 July, 1962  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Modification of the one-sided tracer permeation system was completed. A check was made in which the same disc was run three times. In each run, the disc was removed and replaced so that errors from lack of reproducible sample attachment would be included in the results. Linear regression was applied to 25 points read from each activity curve to yield the slopes of the semilog plots. These slopes, to which the effective diffusivities are directly proportional varied from the average with a maximum deviation of 3.5 per cent. The 95 per cent confidence limits on the line slopes were about 1 per cent of the values of the slopes. While three replicates were insufficient for reliable statistical evaluation, the slope range and comparison of the three slopes are favorable indications of the reproducibility of the method.

Additional runs were made to determine the optimum activity to be used in the permeation system. An activity of approximately 0.5 mc proved adequate to yield a clearly defined diffusion curve. Since the redesigned system included provisions for injection of a reproducible volume of tracer gas, this rough activity was adopted as the standard tracer load. It should be recalled, however, that the method does not require an accurate or known amount of activity.

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July 11, 1962

Several 14.6 w/o Al-U<sub>3</sub>O<sub>8</sub> pellets were run in air to allow motion pictures to be made. These pellets were quenched in water immediately after ignition. X-ray analysis of the quenched pellets indicated a slight decrease in the normal amount of UAl<sub>2</sub> and UAl<sub>3</sub> but no significant qualitative differences from vacuum or argon cooled pellets.

In view of the lack of sensitivity of DTA with the higher aluminum content pellets, a series of tests, based on X-ray analysis, was made to determine the temperature of onset of the reaction. The completed series of pellets will consist of compositions from 6.3 to 65 w/o aluminum heated at 60°F per minute to 1200, 1400, 1600, and 1800°F. The runs completed to date indicate that short-time reactions occur by 1200°F in pellets containing at least 35.7 w/o aluminum and by 1400°F in pellets containing at least 26.6 w/o aluminum.

## II. Future Work

Permeation testing will be begun with silica discs fired under different conditions.

Steam firing of the slip cast fused silica will be resumed with provisions for monitoring the firing temperature.

Reaction studies will be continued in Al-U<sub>3</sub>O<sub>8</sub> pellets of different composition.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
Ceramics Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

August 16, 1962

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 45, Project No. B-153  
Covering the Period from 1 July to 1 August 1962  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Determinations were made of the compressive strength of slip cast fused silica as a function of firing conditions. One inch long sections were cut from 3/4-in. diameter by 5-5/8-in. long transverse test specimens fired at 2000, 2100, 2133, 2166, 2200 and 2300° F for various times. In most cases, at least 45 specimens were used at each firing point. The minimum number of specimens at any firing point was 26. The samples were compression tested on a Tinius Olsen 60-L universal tester employing a spherical bearing block to avoid misalignment. The bearing surfaces were cushioned with cardboard and a loading rate of 4800 lb. per minute was used. The firing conditions enclosed the point of maximum strengthening for all firing temperatures with the exception of 2000° F. These maximum strengths ranged from 20,970 + 830\* psi at a firing time of 48.32 hours and a firing temperature of 2100° F to 25,770 ± 1,490 at 1.79 hours and 2300° F.

Further firings of the slip cast fused silica were made in steam. The firing temperature was first located at which the maximum strength occurred at approximately the same time as in air firing at 2200° F. This temperature proved to be 2075° F. Firings were next made at 2075° F to outline the point of maximum strength. The results from the tests completed to date are summarized in Table I. These data show an interesting contrast to the data from air firings. In the air firings, the maximum strength was approximately 4800 psi at a firing temperature of 2200° F and a firing time of approximately 4 hours. The minimum porosity for the 2200° F air firing was 14.63 per cent. The maximum strength from the steam firings was 5950 psi and the minimum

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\*Interval expected to contain true average within 95 per cent confidence.

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porosity was 11.88 per cent. As opposed to its behavior during air firing, the porosity in steam firing continued to decrease even after the point of maximum strengthening was passed. This indicates a pronounced effect of steam on the sintering rate of cristobalite. Further runs must be made to clarify the apparent inconsistencies in the 8 hour data. Since two mechanisms are operative, increased devitrification and increased cristobalite sintering, the apparent inflection in the bulk properties may prove to be real.

TABLE I

PROPERTIES OF SLIP CAST FUSED SILICA FIRED IN STEAM AT 2075° F

Uncorrected Firing Time	Modulus of Rupture	Porosity*	Bulk* Density	Apparent* Theoretical Density
(hr)	(psi)	(%)	(gm/cc)	(gm/cc)
2	4020	15.07	1.884	2.217
4	4910	14.61	1.896	2.220
6	5950	13.22	1.924	2.216
8	5720	13.63	1.913	2.215
16	2930	11.88	1.974	2.236

\*Air Displacement Values

Expanded studies were begun with the Al-U<sub>3</sub>O<sub>8</sub> thermet system to determine the effect of U<sub>3</sub>O<sub>8</sub> particle size on the ignition characteristics of a 25 w/o Al mixture and to investigate the products formed in pellets of different composition as a function of the maximum pre-ignition temperature reached. These studies are not yet complete enough to show definite trends.

## II. Future Work

Steam firing of the slip cast fused silica will be continued.

Low temperature firing of the slip cast alumina will be resumed.

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Oak Ridge Operations Office

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Particle size and composition studies will be continued with the  
Al-U<sub>3</sub>O<sub>8</sub> thermets.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

September 15, 1962

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 46, Project No. B-153  
Covering the Period from 1 August to 1 September 1962  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Progress in the work with slip cast fused silica was severely hampered during this report period by the breakdown of two principal pieces of equipment. The power supply to the steam firing furnace failed, preventing further work in this area. The exhaust blower in the krypton permeation system also failed. Although this would not interfere with operation of the permeation system, licensing requirements prevented use under these conditions. Repairs are now underway and should be completed during the next report period.

Preparations were begun for milling of a large batch of the alumina slip. A 13-1/2 gallon ball mill was obtained and erected. As soon as a replacement mill collar is delivered, milling will begin. A mill of homogeneous slip will be produced to be used in determination of the alumina firing profile.

In keeping with attempts to extend the Al-U<sub>3</sub>O<sub>8</sub> studies to higher aluminum contents, an evaluation was made of the influence of U<sub>3</sub>O<sub>8</sub> particle size on the ignition characteristics of 25 w/o aluminum compacts. Spencer fused U<sub>3</sub>O<sub>8</sub> was separated into six particle size cuts by screening in a Syntron sieve shaker. Pellets were pressed from mixtures of these U<sub>3</sub>O<sub>8</sub> fractions and Alcoa 140 flake aluminum. Five pellets from each mixture were subjected to differential thermal analysis at a rate of 60° F per minute. Following DTA, the pellets were analyzed by x-ray diffraction. The results of the DTA tests are summarized in Table I.

TABLE I  
IGNITION CHARACTERISTICS OF 25 w/o Al-U<sub>3</sub>O<sub>8</sub> COMPACTS

<u>U<sub>3</sub>O<sub>8</sub></u> <u>Particle Size</u> (mesh)	<u>Ignition</u> <u>Temperature</u> (°F)	<u>Peak</u> <u>Height</u> (mv)	<u>Peak</u> <u>Area</u> (mv-sec)
+100	1800	0.65	25.2
-100 +140	1820	0.54	11.5
-140 +200	1810	0.54	18.5
-200 +270	1830	0.51	15.3
-270 +325	1820	0.58	16.5
-325	1780	0.74	30.0

The results were somewhat different from those obtained previously with 14.6 w/o Al-U<sub>3</sub>O<sub>8</sub> compacts. The lowering in ignition temperature with decreasing particle size of the U<sub>3</sub>O<sub>8</sub> noted with 14.6 w/o aluminum failed to appear in the 25 w/o aluminum compacts. In addition, the peak heights and peak areas obtained from the 25 w/o aluminum compacts showed substantially less particle size dependence than those from the 14.6 w/o aluminum compacts. Although this difference may arise from the somewhat greater volume fraction of aluminum in the 25 w/o pellets, the meaning of these results is not clear. Further studies are planned to compare the two compositions more directly.

## II. Future Work

Following completion of repairs of the steam firing furnace and permeation system, these two phases of the study will be resumed.

Further firings will be made with 14.6 and 25 w/o Al-U<sub>3</sub>O<sub>8</sub> compacts to resolve the apparent differences in behavior.

~~Respectfully~~ submitted,

*J. D. Fleming*  
Senior Investigator

Approved:

J. D. Walton, Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

October 15, 1962

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 47, Project No. B-153  
Covering the Period from 1 September to 1 October 1962  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Repairs of the permeation and steam firing systems were completed.

Data analysis was completed in the study of the influence of firing conditions on the bulk density of slip cast fused silica. The slopes of the curves of bulk density vs. corrected firing time followed an Arrhenius variation with temperature. Although the Arrhenius plot of these data is not purported to represent any particular solid state process, it is interesting to compare the resulting activation energy of 69 kcal/mole with the 51 kcal/mole reported for the devitrification of amorphous silica<sup>1</sup>. Further studies are planned to clarify the meaning of these results.

Investigations were begun to determine the nature of the exothermic peaks observed in Al-U<sub>3</sub>O<sub>8</sub> compacts at about 1200° F. In order to minimize the masking effects of the endotherm resulting from melting of the aluminum, a new standard pellet was used in place of the alumina pellet previously employed. This pellet consisted of aluminum with alumina in the same volume per cent as that of the U<sub>3</sub>O<sub>8</sub> in the unknown pellet. This standard pellet produced much better curves than the alumina standard and apparently was successful in eliminating the aluminum melting endotherm.

Using the new standard, 14.6 w/o aluminum compacts with Spencer fused U<sub>3</sub>O<sub>8</sub> were subjected to DTA tests at 60° F per minute. Exotherms appeared at approximately 1250° F in all cases. Further studies must be made, before placing too much emphasis on these results, to be sure that the exotherm is genuine rather than due to the standard containing more aluminum than the unknown. The strong necessity for such precautions when using reactive standards is obvious.

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<sup>1</sup>Verduch, A. G., "Kinetics of Cristobalite Formation from Silicic Acid",  
J. Am. Ceram. Soc. 41 427-32 (1958).

October 15, 1962

Runs were begun to compare the reactivity of "dead-burned" Y-12  $U_3O_8$ , furnished by ORNL, with Spencer fused  $U_3O_8$ . While only two samples of a 14.6 w/o aluminum content have been run, the initial indications were that the two oxides are quite similar. The Y-12 oxide showed an exotherm at 1220° F and ignition at 1840° F. The fused oxide showed an exotherm at 1250° F and ignition at 1810° F. The Y-12 oxide gave a much greater peak height and area than the fused oxide but this is felt to be due to inadvertent use of a substandard weight fused oxide pellet.

## II. Future Work

Permeation tests of the slip cast fused silica will be resumed.

Steam firing of slip cast fused silica will be continued.

DTA and x-ray tests will be continued to clarify the 1200° F exotherms in the Al- $U_3O_8$  compacts.

Comparative studies of Y-12 and Spencer fused  $U_3O_8$  will be continued.

Modifications will be made to lend additional sensitivity to the DTA system. The modified system will be used in investigations of high aluminum compacts.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
High Temperature Materials Branch

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# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

November 16, 1962

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 48, Project No. B-153  
Covering the Period from 1 October to 1 November 1962  
Contract No. AT-(40-1)-2483.

Gentlemen:

## I. Experimental Progress

The DTA system used for study of ignition in low aluminum Al-U<sub>3</sub>O<sub>8</sub> compacts was of such low sensitivity that reactions could not be detected in composites containing more than 40 w/o aluminum. Low output platinum-rhodium thermocouples were used in order to withstand the high temperatures generated during ignition. The thermocouples were enclosed by alumina spaghetti, sealed on one end, to avoid shorting by aluminum evaporated from the igniting pellet. This design produced very low sensitivity, suitable for study of low aluminum composites but not for investigations of aluminum rich composites.

In order to provide, as economically and rapidly as possible, a more suitable system for studying reactions in high aluminum composites, the original thermocouple arrangement was altered in one testing furnace. Conax packing glands were fitted so that bare chromel-alumel wire could be used instead of the integral clad and insulated thermocouple assemblies. The standard and unknown pellet thermocouples were not covered although the pellets were held slightly away from the thermocouples by short lengths of alumina spaghetti. The platinum-rhodium furnace control thermocouple was not changed.

The modified DTA system was checked by running several 25 w/o Al-U<sub>3</sub>O<sub>8</sub> pellets. The oxide used was "dead-burned" Y-12 U<sub>3</sub>O<sub>8</sub> supplied by the Metals and Ceramics Division, Oak Ridge National Laboratory. The system operated satisfactorily and seemed to be about an order of magnitude more sensitive than before modification.

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November 16, 1962

A series of 50 w/o Al-U<sub>3</sub>O<sub>8</sub> pellets was pressed from Y-12 U<sub>3</sub>O<sub>8</sub>. Several pellets were tested at a heating rate of 60° F per minute in the modified furnace under a pressure of 15 psig of argon. A pressed alumina standard was used. The DTA chart showed wide fluctuations on the differential axis. No conclusions whatever could be reached about low temperature reactions, although an apparent reaction was seen at approximately 1780° F.

Some of the difficulty with the alumina standard was thought to be due to the much higher thermal conductivity in the 50 w/o pellets compared with the low aluminum pellets studied previously. An ideal standard would have the same thermal diffusivity as the unknown and would contain the same amount of aluminum. This would cancel the aluminum melting endotherm on the DTA chart and, in theory, render low temperature reactions more obvious. While optimization of the standard would be a lengthy program, obviously beyond the scope of this study, a brief survey of various standards was begun. Standards to be evaluated include alumina, fired Al-U<sub>3</sub>O<sub>8</sub> pellets, and Al-Al<sub>2</sub>O<sub>3</sub> composites with the Al<sub>2</sub>O<sub>3</sub> present in the same volume per cent as the U<sub>3</sub>O<sub>8</sub> in the unknown.

Runs of 50 w/o Al-U<sub>3</sub>O<sub>8</sub> pellets were begun in the modified furnace against the above standards. Apparent reactions were indicated by fairly sharp DTA peaks in the range of 1700-1840° F regardless of the standard used. The aluminum endotherm was not successfully eliminated by any standard and the presence or absence of lower temperature reactions was impossible to discern.

While the planned DTA tests are far from complete, the results obtained so far are both promising and disappointing. DTA tests may prove capable of demonstrating the existence of high temperature reactions but, in high aluminum composites, reliable indications concerning low temperature behavior will be extremely difficult to obtain. Successful suppression of the aluminum melting endotherm is very doubtful.

## II. Future Work

Brief studies will be made of standards for use in DTA testing of high aluminum composites.

Testing of 50-65 w/o Al-U<sub>3</sub>O<sub>8</sub> composites will be continued.

Statistical comparisons of Y-12 and Spencer U<sub>3</sub>O<sub>8</sub> will be made.

~~Respectfully~~ submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

December 12, 1962

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 49, Project No. B-153  
Covering the Period from 1 November to 1 December 1962  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

A 3/8-in. thick plate of Al-U<sub>3</sub>O<sub>8</sub> dispersion was received from the Oak Ridge National Laboratory for testing. The composition of the dispersion was 33.79 w/o U<sub>3</sub>O<sub>8</sub>, 66.07 w/o X-800 aluminum, and 0.14 w/o B<sub>4</sub>C. Dead-burned Y-12 U<sub>3</sub>O<sub>8</sub> was used in the fabrication of the plate, probably from the same batch as the Y-12 oxide used in the pressed compacts discussed in the previous monthly letter report. The plate was rolled at 500° C with an 8:1 reduction and a 15 per cent cross roll.

A reference sample was cut from the as-received plate and half of the plate was annealed at 500° C for one hour in a vacuum. After the anneal a second reference sample was cut and 3/8-inch square pellets were cut for differential thermal analysis.

Two DTA runs were made to 2000° F at 60° F per minute using unfired samples on both the standard and unknown thermocouples. The DTA curves deviated from a straight line in the range of 1200 - 1400° F but no high temperature exotherm was observed. These pellets were retained for use as standards for subsequent tests.

DTA runs were made at 60° F per minute to 1400° F and 1900° F using previously fired samples as standards. Reasonably good curves were obtained with very noticeable thermal differentials at 1200 - 1400° F and at 1700 - 1800° F. The 1700 - 1800° F differentials could be distinguished clearly to be exotherms. The 1200 - 1400° F differentials could not be identified definitely but appeared to be combinations of an exotherm with the normal aluminum melting endotherm.

December 12, 1962


One specimen from each of the as-received, annealed 1400° F fired, and 1900° F fired groups was subjected to x-ray diffraction. The as-received sample showed very strong aluminum and  $U_3O_8$  peaks, a few weak  $UO_2$  peaks, and significant low angle strain scattering. The vacuum annealed sample showed disappearance of the strain scattering hump and some clear, but not extensive, growth of  $UO_2$ . No significant changes were noticed in the aluminum and  $U_3O_8$  peaks. The sample heated to 1400° F showed wide-spread change. The aluminum and  $U_3O_8$  peaks were grossly diminished and the  $UO_2$  peaks showed very pronounced growth. The sample heated to 1900° F showed further change in that quite prominent  $UAl_4$  peaks and a few  $Al_2O_3$  peaks were found and the  $UO_2$  and aluminum peaks were decreased. The  $U_3O_8$  peaks were still barely discernible but had almost completely disappeared.

## II. Future Work


Samples cut from the Al- $U_3O_8$  plate will be DTA tested and heated to 1000, 1200, 1400, and 1600° F for x-ray and metallographic examination.

Test runs will be begun with compacts pressed from aluminum and hydrothermal ORNL  $UO_2$ .

Respectfully submitted,

 D. D. Fleming  
Senior Investigator

Approved:

 J. D. Walton, Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

January 15, 1963

*Sent to Fleming  
1/23/63*

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 50, Project No. B-153  
Covering the Period from 1 December 1962 to 1 January 1963  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

The final series of runs was begun in the determination of the high temperature tensile strength of slip cast fused silica. The testing procedure involves placing the silica ring in the preheated tensile test furnace and holding for thermal equilibration prior to loading. A study was made to verify the assumption that the specimen is in thermal equilibrium by the time the testing furnace returns to the testing temperature. Three sets of 12 rings were fired at 2200° F for an uncorrected firing time of two hours. Four rings from each firing were broken as soon as possible, approximately three minutes, after insertion into the furnace, four after return of the furnace to the testing temperature of 2000° F, and four five minutes after the furnace returned to 2000° F. The results were subjected to the two factor analysis of variance summarized in Table I.

TABLE I  
ANALYSIS OF VARIANCE OF RING TEST DATA

<u>Source of Estimate</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square Estimate</u>	<u>F</u>
Between Firings	207,239	2	103,620	6.36***
Between Warm-ups	100,643	2	50,322	3.09
Interactions	150,535	4	37,634	2.31
Error	440,201	27	16,304	-

(Continued)

TABLE I (Continued)  
ANALYSIS OF VARIANCE OF RING TEST DATA

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$F_{0.05, 2/27} = 3.35$	$F_{0.05, 4/27} = 2.73$
$F_{0.01, 2/27} = 5.49$	
$F_{0.005, 2/27} = 6.49$	

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The time allowed for reheating prior to testing failed to show significance at the 95 per cent level of confidence. This is not surprising since the point of maximum stress in the ring is at an exposed surface and a rapid thermal equilibration at this point would be expected. In order to provide a uniform basis for future testing, the ring furnace will be allowed to return to the testing temperature prior to loading.

Several studies were begun to provide further data for high aluminum content Al-U<sub>3</sub>O<sub>8</sub> composites. These studies are summarized below:

a. Influence of Composition.

Compacts containing 35, 40, 45, and 50 w/o U<sub>3</sub>O<sub>8</sub> formulated from Oak Ridge "Dead-burned" U<sub>3</sub>O<sub>8</sub> and Alcoa 140 atomized aluminum. Subjected to DTA through the firing point, x-ray analysis, and metallography.

b. Influence of Oxide Source.

Compacts containing 75 w/o U<sub>3</sub>O<sub>8</sub> formulated from "Dead-burned" and Spencer fused U<sub>3</sub>O<sub>8</sub>. Subjected to DTA for comparison of reactivity through statistical analysis of firing characteristics.

c. Reactions in ATR Plate.

Specimens cut from ATR composition plate furnished by ORNL. DTA tested to temperatures of approximately 1000, 1200, 1400, and 1600° F and through the firing point. X-ray analysis and metallography.

d. Comparison of UO<sub>2</sub> with U<sub>3</sub>O<sub>8</sub>.

Compacts containing 35 w/o UO<sub>2</sub> prepared using Alcoa 140 atomized aluminum and ORNL Hydrothermal UO<sub>2</sub>. DTA tested through the firing point. X-ray analysis and metallography.

January 15, 1963

The four studies are being carried out concurrently. DTA tests on all four are better than 50 per cent complete. Additional personnel are being assigned to the x-ray analysis to decrease the delay in this phase of the studies. Preliminary results are expected from all studies during the month of February.

## II. Future Work

High temperature tensile tests of the slip cast fused silica will be continued.

Steam firing profiles will be determined for the slip cast fused silica.

Studies in high aluminum Al- $U_3O_8$  and Al- $UO_2$  compacts will be continued.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
High Temperature Materials Branch

**GEORGIA INSTITUTE OF TECHNOLOGY**  
**ENGINEERING EXPERIMENT STATION**  
**ATLANTA 13, GEORGIA**

February 20, 1963

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 51, Project No. B-153  
Covering the Period from 1 January to 1 February 1963  
Contract No. AT-(40-1)-2483

Gentlemen:

I. Experimental Progress

Prior to undertaking the task of fabricating an Inconel chamber for steam firing silica in a bottom loading furnace, attempts were made to improve the steam flow control in the tube furnace. A compressed air controlled water ballast tank was inserted in the flow line and a constant water pressure was maintained during firing. Water was admitted to the tube furnace at a rate of 0.72 pounds per hour, regulated by a rotometer. Three-quarter-inch diameter slip cast fused silica bars were fired at temperatures of 2000, 2100, and 2200° F for varying periods of time sufficient to enclose the maximum strength. The fired bars were checked for porosity, bulk density, and theoretical density using the air porosimeter and were tested for modulus of rupture.

The steam firings with the modified water flow system were quite reproducible. The results of the tests continued to show remarkable differences between steam and air firing. In all cases, the steam firing produced much more rapid strengthening, lower porosity, and higher bulk density. At 2100° F, for instance, a maximum strength of 4200 psi was reached in air firing at a time of 48 hours. In steam firing at 2100° F, a maximum strength of 4500 psi was reached at 8 hours. The porosity differences are equally striking. In air firing, the minimum porosity attained was approximately 14.2 per cent. In steam firing, the minimum porosity obtained in the longest 2200° F run was 11.5 per cent but the porosity showed no sign of reaching a minimum at this point. The sintering behavior in steam is different from that in air. In air firing, the bulk density increases as the logarithm of firing time but, in steam, the increase is linear with time. This implies that the sintering mechanism in steam firing is viscous flow. From the densification data, an activation energy of 110 kcal/mole was calculated for firing slip cast fused silica in steam at 0.72 pounds per hour.

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February 20, 1963

The first set of x-ray data was obtained for the ATR Al-U<sub>3</sub>O<sub>8</sub> dispersion heated to temperatures from 1000 to 1830° F. The specimen series consisted of the as-received plate, plate vacuum annealed for one hour at 500° C, and annealed plate heated to 1000, 1200, 1400, 1600, and 1830° F at 60° F per minute and furnace cooled. With increasing heat treatment, both the U<sub>3</sub>O<sub>8</sub> and aluminum showed consistent decreases although an orientation shift in the aluminum made quantitative comparison difficult. The UO<sub>2</sub> was not as well behaved, showing a substantial initial increase upon annealing followed by a great decrease in the 1000° F specimen and erratic behavior in the others. A small UAl<sub>4</sub> peak was observed in the 1000° F specimen but not again until 1600° F when both UAl<sub>3</sub> and UAl<sub>4</sub> were detected. In the 1830° F specimen, strong diffraction traces for UAl<sub>3</sub> and UAl<sub>4</sub> were obtained. Traces for Al<sub>2</sub>O<sub>3</sub> were first noted at 1200-1400° F, becoming stronger at 1600° F and quite prominent at 1830° F. Residual U<sub>3</sub>O<sub>8</sub> was detected in appreciable amounts in all specimens.

The initial x-ray results support the suggestion of a two stage reaction, at least at lower temperatures. Between approximately 900 and 1700° F, U<sub>3</sub>O<sub>8</sub> appears to be reduced to UO<sub>2</sub>. At approximately 1700° F, further reduction of the UO<sub>2</sub> to UAl<sub>3</sub> and UAl<sub>4</sub> occurs. The possibility of direct reduction of U<sub>3</sub>O<sub>8</sub> to U-Al intermetallics at high temperatures cannot be evaluated from these data.

The behavior of the UO<sub>2</sub> is not clear at this point. Since all heated specimens showed decreases in U<sub>3</sub>O<sub>8</sub> and UO<sub>2</sub> from the annealed specimen, formation of some U-Al intermetallics would appear certain in all cases. Actually, however, only the 1000, 1600, and 1830° F specimens gave x-ray traces for the compounds. This would seem to indicate either significant structural non-uniformity in the rolled plate, which metallography denies, or a poor x-ray detection sensitivity for the U-Al intermetallics. Since only one sample has been studied at each condition, this cannot yet be verified.

## II. Future Work

Steam firing of slip cast fused silica will be continued at different steam concentrations.

X-ray and metallographic studies of rolled Al-U<sub>3</sub>O<sub>8</sub> of ATR composition will be continued.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

March 19, 1963

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 52, Project No. B-153  
Covering the Period from 1 February to 1 March 1963  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Firing contours of silica under one atm. abs. of steam were completed. Firings were made in sets of 11 3/4-in. diameter by 5-5/8 in. long bars. Single firings were made at 2000° F for 66 and 68-1/4 hours and at 2100° F for 13-3/4 hours. Duplicate firings were made at 2000° F for 6-1/4, 24, and 40 hours; at 2100° F for 1, 2, 4, 6, 8, 12, and 16 hours; and at 2200° F for 1, 2, 4, and 8 hours. Prior to firing, the furnace tube was evacuated and backfilled with argon four times. The tube was then inserted into the preheated furnace and water was introduced at 0.72 pounds per hour. The steam was allowed to escape through a 1/4-in. pipe at the hot end of the tube. Although a pressure gauge was not used, rough calculations showed the pressure drop to be negligible so that the tube pressure was very nearly atmospheric.

Under one atmosphere of steam, the strength profiles and contours were very similar in shape to those obtained in air firing. The faster overall strengthening kinetics previously observed continued to apply in the extended firings. These supplementary firings did clarify one point, however. The air firings showed a faster initial sintering rate but the rate began to fall soon after the shortest sintering runs. The steam sintering rate sustained a high value and, for strengths of practical magnitude, showed a higher averaged value than the air rate. The porosities measured in the steam firings continued to show a decrease, reaching a value of 11.5 per cent in the longest 2200° F run. Still no indication of a porosity minimum was obtained.

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FORMAT 10-4 1963 BY

March 19, 1963

Firing of slip cast fused silica was begun using two atm. abs. steam. While these runs are not yet complete, the preliminary results are highly encouraging. The strengthening rate appears approximately twice that in one atm. steam. A maximum strength of 6000 psi appears likely compared with 4500 psi for one atm. steam. In addition, the strengthening profile appeared much more flat than in one atm. steam or in air, indicating improved firing uniformity.

Modification of the dynamic x-ray diffraction system was begun to permit investigation of reaction kinetics in ATR fuel compacts. Test runs are expected to be begun during the next month.

Further DTA runs were made with ATR compacts using bare standard thermocouples and graphite standards. These runs were made principally for the purpose of defining the behavior of the compacts in the range of 1200° F. While the DTA traces were not very satisfactory over the entire temperature range, the 1200° F region appeared fairly clear. According to these curves, no obvious reaction exotherm appears in this region. This result is not in complete agreement with the results of x-ray diffraction and metallography of the test pellets. The latter examinations showed strong evidence of substantial reaction. Further runs are underway to clarify the results of the three analytical procedures.

## II. Future Work

Further firings of slip cast fused silica will be made in two atm. abs. steam.

Test runs of ATR compacts will be made in the modified dynamic high temperature x-ray diffraction unit.

Examination of the 1200° F reactions in ATR compacts will be continued using DTA, x-ray diffraction, and metallography.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

April 10, 1963

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 53, Project No. B-153  
Covering the Period from 1 March to 1 April 1963  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Firing of slip cast silica was continued under steam at two atm. absolute pressure. Based on the data obtained to date from these runs, the higher steam concentration appears more effective in increasing the sintering kinetics at the higher firing temperatures. At 2000° F, the incomplete data now available indicate slightly, but probably not significantly, higher kinetics with two atm. steam than with one atm. steam. At 2100° F, however, the two atm. firings appear to show significantly higher sintering kinetics. The maximum strength attained in two atm. firing was approximately 6400 psi at a firing time of 6 hr. compared with 4600 psi after a firing time of 10 hr. under one atm. steam.

As with the firings under one atm. steam, the bulk density of the silica showed a linear increase with time, indicating a viscous flow sintering mechanism. The activation energy for two atm. firing has not yet been determined but will probably be higher than for firing under one atm. of steam. No sign of approach to minimum porosity has yet been obtained.

Modification of the high temperature x-ray diffraction system was completed. A Kanthal wound furnace was constructed from silica foam. An alumina slab was slip cast to serve as support for the aluminum-U<sub>3</sub>O<sub>8</sub> sample for reaction rate determinations at temperatures above the melting point of aluminum. Although the inert gas chamber for the furnace has not yet been completed, several trial runs were made in air to evaluate the performance of the furnace and diffraction system. Repetitive scans were made of several peaks including strong peaks of U<sub>3</sub>O<sub>8</sub> and UO<sub>2</sub>. At temperatures of 1500 to 1800° F, the system performance was entirely satisfactory. No difficulties which could not be accommodated were encountered from thermal noise, warping and shifting of the specimen, or background increase from x-ray scattering by the liquid aluminum.

April 10, 1963

Since the  $\text{Al}_2\text{O}_3$  surface film on the specimen grew at an undetermined rate, no quantitative significance could be attached to the observed decrease in  $\text{U}_3\text{O}_8$  peak intensity. The inert atmosphere chamber should be completed early during the next month and rate determinations will be begun.

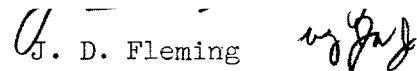
## II. Future Work

Two atm. steam firing of slip cast fused silica will be begun. The viscous flow sintering activation energy will be determined.


Determination of the reaction rates in  $\text{Al-U}_3\text{O}_8$  composites will be begun as soon as the inert gas chamber for the x-ray furnace is completed.

Initial surveys will be made to evaluate the feasibility of DTA calorimetry for the  $\text{Al-U}_3\text{O}_8$  composites using the aluminum endotherm as an internal standard.

Respectfully submitted:

  
J. D. Fleming  
Senior Investigator

Approved:

 J. D. Walton, Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

May 21, 1963

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 54, Project No. B-153  
Covering the Period from 1 April to 1 May 1963  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

Consideration of the probable mechanism of the initial stages of devitrification in slip cast fused silica indicated that the cristobalite content should show a cubic variation with time. Preliminary x-ray diffraction data for air fired and steam fired specimens appeared to follow this expected behavior fairly well. Based on this treatment of the data, the initial cristobalite content of the slip was found to be approximately 0.5 per cent. Both the steam and air data were in agreement on this point. While the air firing data were too limited for further analysis, the steam data permitted determination of the activation energy for devitrification. In steam of one atmosphere absolute, the early devitrification activation energy is approximately 98 kcal per mole.

A study was made of the influences of pressure application and mold vibration during slip casting of fused silica. Specimens, 3/4-in. in diameter by 5-5/8-in. long, were cast in random order under pressures of 0, 20, 40, and 60 psig with 60 cps axial vibrations of 0, 0.010, 0.012, and 0.015-in. amplitude. A new mold was used for each casting. Following drying of the cast specimens, the bulk properties were determined by air displacement. The casting time was decreased by the application of pressure from approximately 150 min. at 0 psig to approximately 17 min. at 60 psig. This decrease in casting time was obtained at the cost of a decrease in cast bulk density from 1.854 to 1.846 gm. per cc. Vibration of the mold during casting partially offset this density decrease. At

May 14, 1963

the highest vibration amplitude at 60 psig, the cast density was returned to 1.849 psig with no apparent increase in casting time. Determination of the modulus of rupture was begun using the dry pressure-vibration cast specimens.

Investigations were begun to determine the feasibility of Al-U<sub>3</sub>O<sub>8</sub> reaction calorimetry by differential thermal analysis. Pellets were machined from spectrographic graphite rods to serve as standards for DTA of ATR specimens. The graphite pellets were vacuum heated at 2100° F for several hours to remove any volatile contaminants. Two trial DTA runs were made using ATR unknowns and graphite standards. The DTA curves were quite similar to those obtained in the past using fired ATR specimens as standards except, of course, that the aluminum therms were larger. Establishment of a base line on the DTA curve proved quite difficult with only two specimens. From these preliminary curves, however, estimated reaction energy release appeared to be at least 0.07 Mw-sec per kg. of Al-U<sub>3</sub>O<sub>8</sub> dispersion. The only value of this figure, which could easily be in error by a factor of three or more, is in indicating that the result is at least reasonable and that the method is worthy of further study.

A rather serious set-back was encountered in the high temperature x-ray studies of reaction kinetics in the ATR dispersion. The counting tube on the diffraction system became inoperative, necessitating replacement. The counting tube geometry, unfortunately, had been changed by Siemens since procurement of the diffraction system. As a result, an adapter had to be designed and constructed to fit the new tube to the old detector head. This has resulted in a significant delay, but the system should be back in operation in the near future.

## II. Future Work

The firing of slip cast fused silica under two atmospheres absolute of steam will be completed.

Investigations of DTA calorimetry of ATR dispersions will be continued.

As soon as the x-ray system is repaired, kinetics studies will be resumed.

Respectfully submitted:

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
High Temperature Materials Branch

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

JUN 21 1963

June 10, 1963

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 55, Project No. B-153  
Covering the Period from 1 May to 1 June 1963  
Contract No. AT-(40-1)-2483

Gentlemen:

I. Experimental Progress

Studies were completed to permit a comparison of the bulk density changes in slip cast fused silica sintered in air and in steam. Firings were made in one atmosphere air, one atmosphere steam, and two atmosphere steam. Although the initial bulk densification rate in air was higher than in one atmosphere steam, the rate was maintained constant up to the point of maximum strength in steam and decreased continuously in air. 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 in air, 8.7 hours in one atmosphere steam, and four hours for two atmosphere steam. At a time corresponding closely to that required for maximum strength development in steam, an abrupt decrease in densification rate was noted. This was tentatively attributed to blockage of viscous flow at the particle surfaces by completion of a continuous devitrified layer. This effect would be masked in air firing since the probable sintering mechanism, plastic flow, produces a continuous sintering rate decrease.

Modulus of rupture testing was completed with the pressure-vibration cast fused silica bars. Pressure application during casting consistently decreased cast density and green strength while mold vibration during casting increased both. At the maximum vibration amplitude, without pressure application, the green modulus of rupture was increased from 160 psi to 197 psi. Pressure application above 20 psig returned the green modulus of rupture to 160 psi, even with maximum mold vibration.

Rough measurements were made of the load bearing capacity of molten ATR fuel specimens. An approximately 90-mil thick specimen was supported on the

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end of a 1/4-in. tube passing into a DTA furnace chamber. The tube was valved so that a partial vacuum could be produced and a differential pressure generated between the furnace body and the tube-side of the ATR specimen. The specimen was heated to the desired testing temperature and allowed to equilibrate. A pressure differential was then generated across the specimen which sealed the tube at or below the melting point of aluminum. The pressure differential was then increased slowly, over a period of about a minute, until the specimen sagged visibly. Specimens at 1350 and 1700° F sagged when the differential reached an average of about 0.8 psi. Specimens which were allowed to react prior to pressure application failed to sag under 4 psi, the maximum obtainable in the system, at 1860° F. Metallographic examination of the sag specimens was begun.

Following restoration of the high temperature x-ray diffraction system to operation, difficulty was encountered from the Al-U<sub>3</sub>O<sub>8</sub> specimen bloating during the test. This bloating was sufficient to block the x-ray beam and halt the test. Attempts are now under way to determine and correct the cause of this bloating.

## II. Future Work

Work will be concentrated on the last series of ring tests to determine the high temperature tensile strength of slip cast fused silica.

Studies will be continued to evaluate the feasibility of DTA calorimetry of Al-U<sub>3</sub>O<sub>8</sub> reactions.

The ATR sag test specimens will be examined in an attempt to identify the mode of failure.

Attempts will be made to eliminate sample bloating in the high temperature x-ray investigation of Al-U<sub>3</sub>O<sub>8</sub> reaction kinetics.

Respectfully submitted:

W. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

July 30, 1963

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 56, Project No. B-153  
Covering the Period from 1 June to 1 July 1963  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

High temperature tensile tests were carried out using ring specimens fired at 2166°F for 8.5 hours and at 2200°F for 3.3 hours. The rings for these tests were cast in plaster molds rotating at approximately 36 rpm. In approximately five hours, each mold produced a 3-in. outside diameter, 1-1/2-in. nominal inside diameter cylinder 12-in. long. The castings were air dried in the molds overnight, removed, dried to constant weight at 130°F, dried at 230°F for 16 hours, bisque fired at 1800°F for two hours, and sawed into 1-in. thick rings. After being dried at 230°F for at least three hours, the rings were fired.

Tensile tests were carried out at room temperature, 400, 800, 1200, 1600, and 2000°F using specimens fired as described above. The room temperature strengths were approximately 2600 psi for the rings fired at 2166°F and 3400 psi for those fired at 2200°F. With increasing testing temperature, the strengths of both types of rings increased rapidly, doubling by approximately 1200°F. The strengths of the rings fired at both 2166 and 2200°F seemed to approach the same level at approximately 2000°F. Determination of a representative strength at 2000°F proved impossible since 60 per cent of the specimens failed to break under a stress of about 7500 psi, the working limit of the ring tester. While the lower temperature tests are being completed, the best method of obtaining strengths at 2000°F will be selected. This will be either refiring of rings of different size or, more likely, replacement of the hydraulic working cylinder with one of larger size.

The high temperature x-ray diffraction system was returned to service and the studies of Al-U<sub>3</sub>O<sub>8</sub> reaction kinetics were resumed. Since the supply

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July 30, 1963

of rolled ATR plate is almost exhausted, these runs are now being made with powder metallurgy specimens until a new supply of plate is received. The powder metallurgy specimens seem to display the same behavior as the rolled specimens and should be quite adequate for system calibration. In the first runs, the pellets are being examined by optical metallography and analyzed chemically for  $\text{Al}_2\text{O}_3$ . The results of these studies will be correlated with the x-ray diffraction traces to provide concentration axis calibration for the rate curves.

### II. Future Work

High temperature tensile testing of slip cast fused silica will be continued.

Reaction rate measurements will be continued in ATR composition  $\text{Al-U}_3\text{O}_8$  compacts.

Attempts will be made to develop a method for DTA calorimetry of  $\text{Al-U}_3\text{O}_8$  reactions.

Respectfully submitted:

*James W. Johnson* ✓  
Assistant Project Director

Approved:

J. D. Walton, Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

August 15, 1963

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 57, ~~Project No. B-153~~  
Covering the Period from 1 July to 1 August 1963  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

High temperature ring tensile testing of slip cast fused silica was continued. Tests to 1600° F were completed with rings fired for 19 hours at 2133° F, 8.5 hours at 2166° F, and 3.3 hours at 2200° F, the firing conditions for maximum cold strength. The strength increased with testing temperature in a consistent manner, showing approximately the same rate of change for all three initial firing conditions. The tensile strength showed a roughly linear increase from approximately 3000 psi at room temperature to approximately 6500 psi at 1600° F.

Tensile tests were also made to 1600° F with rings underfired for 2 hours at 2200° F. These rings showed much the same strength characteristics as the optimally fired rings.

The supply of rolled ATR plate was completely exhausted. Until a new plate is received, efforts to determine the kinetics of Al-U<sub>3</sub>O<sub>8</sub> will be concentrated on a study of the U<sub>3</sub>O<sub>8</sub> particle size effects. In order to cover a particle size range including that of the rolled ATR plate, a brief determination of the U<sub>3</sub>O<sub>8</sub> particle size in a sample of the plate is being made. This determination is being made by optical counting of the oxide remaining after caustic dissolution of the aluminum alloy matrix. The results will be compiled by computer analysis.

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August 15, 1963

Metallographic analysis of the Al-U<sub>3</sub>O<sub>8</sub> specimens from the sag test is being continued. The results of this analysis will be reported in the next quarterly report.

II. Future Work

High temperature tensile testing of slip cast fused silica will be extended to 2000° F.

Measurements will be made of the reaction kinetics in Al-U<sub>3</sub>O<sub>8</sub> compacts with different U<sub>3</sub>O<sub>8</sub> particle sizes.

Metallography of the ATR sag specimens will be continued.

Respectfully submitted:

J. D. Fleming  
Senior Investigator

Approved: \_\_\_\_\_

J. D. Walton, Head      y q'  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

September 16, 1963

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 58, Project No. B-153  
Covering the Period from 1 August to 1 September 1963  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Progress

High temperature ring tensile tests were completed for all but one group of firings. The groups tested include a profile of 2200° F firings at 0.5, 2, 3.3, and 5 hours and firings, for maximum room temperature strength, at 2133° F for 19 hours, 2166° F for 8.5 hours, and 2200° F for 3.3 hours. The optimum fired rings showed essentially the same response to the testing temperature, an approximately linear increase in strength with temperature. The underfired rings showed a small increase in strength with increasing testing temperature, but only above a testing temperature of 1200° F. The rings fired at 2200° F for 3.3 hours showed an increase in strength from 3400 psi at room temperature to 8000 psi at 2000° F. Those underfired at 2200° F for 0.5 hours showed an increase from 2300 psi at room temperature to 3700 psi at 2000° F.

The results of electron microprobe analyses of several fired ATR specimens were obtained from Advanced Metals Research. The analyses were quite similar to those of powder metallurgy specimens examined earlier. The principal phases detected were  $UO_2$ ,  $UAl_2$ , and  $UAl_3$ . The ATR specimens differed from the lower aluminum content powder metallurgy specimens in that the  $UO_2$  appeared oxygen deficient. In addition, a few precipitates of iron-manganese were detected.

Different methods for relief etching the ATR specimens were studied. The most promising appears to be extended exposure to a magnesium oxide slurry in a Syntron bowl polisher. Specimens

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September 16, 1963

treated in this manner show clear relief of  $U_3O_8$  and  $Al_2O_3$  areas and probable relief of U-Al intermetallic compounds. Systematic studies were begun to clarify the effects of this etching procedure.

Dynamic x-ray diffraction studies were continued in an investigation of the influence of  $U_3O_8$  particle size on the reaction kinetics of powder metallurgy Al- $U_3O_8$  compacts.

## II. Future Work

The final ring tensile tests of slip-cast fused silica will be completed.

Brief studies of foamed fused silica will be begun.

Magnesium oxide relief etching of ATR specimens will be studied further.

Studies of reaction kinetics in Al- $U_3O_8$  compacts will be continued using metallography and dynamic x-ray diffraction.

Respectfully submitted:

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Jr., Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

October 14, 1963

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 59, Project B-153  
Covering the Period from 1 September to 1 October 1963  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Work

During the past month the last high temperature tensile strength measurements were completed using slip-cast fused silica. Earlier tests indicated that the tensile strength of optimum fired or underfired slip-cast fused silica increases with testing temperature, presumably as the result of the healing of firing defects. In the later runs with overfired silica, a similar defect healing tendency was observed. In rings fired for 8 hours at 2200° F, the tensile strength increased from 1700 psi at room temperature to 3500 psi at 2000° F.

With the exception of a few isolated studies, the work with slip-cast fused silica is now complete. Data reduction and compilation for the final report on this task are now under way.

The new supply of rolled ATR plate was received. Characterization of the as-received plate was begun. Samples were cut from each plate in three positions which appeared, from the radiographs, to be relatively uniform in U<sub>3</sub>O<sub>8</sub> distribution. These samples will be subjected to metallography, x-ray diffraction, and chemical analysis. Some samples will also be dissolved and the U<sub>3</sub>O<sub>8</sub> powder will be recovered for particle size analysis.



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Page 2

II. Future Work

Data compilation will be continued for slip-cast fused silica topical report.

Reaction kinetics studies will be continued using the new ATR dispersion.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

✓ J. D. Walton, Jr., Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA 30332

November 14, 1963

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 60, Project ~~B-153~~  
Covering the Period from 1 October 1963 to 1 November 1963  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Work

With the completion of the experimental work on slip-cast fused silica, compilation of data for the final topical report was begun. The literature survey supplement was begun.

Arrangements were made to secure samples of foamed fused silica from Glasrock Products Inc. for the limited test to be carried out on this material. It is expected that these samples will be obtained by approximately January 1, 1964 and the tests will be completed as soon after as is convenient.

With the receipt of the new ATR fuel plate, efforts were begun to complete the determination of reaction kinetics of Al-U<sub>3</sub>O<sub>8</sub> dispersions by high temperature dynamic x-ray diffraction studies. While the low temperature, short time runs produced no unforeseen difficulties, efforts to extend to higher temperatures or longer times produced significant macroscopic blistering and swelling in the test specimens. The as-received material showed slightly higher Al<sub>2</sub>O<sub>3</sub> and UO<sub>2</sub> contents than the original ATR fuel plate. The new ATR fuel plate also showed a few relatively small diffraction peaks which did not appear in the original ATR plate. These peaks have not yet been identified. Microstructures of the two plates did not appear to be appreciably different. A detailed review of the sample preparation and handling techniques at the Oak Ridge National Laboratory and at Georgia Tech failed to show any apparent differences between the old and new ATR plate.

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Efforts were begun to eliminate the swelling and blistering by suitable vacuum annealing. Annealing for one hour at 1100° F and one hour at 1150° F produced a very substantial decrease in the incidence of swelling and blistering. In samples annealed in this manner, the incidence of swelling and blistering was reduced from approximately 100 per cent to approximately 20 per cent. Annealing at 1200° F for one hour produced marked blistering in the samples. More detailed tests were begun to determine the cause and methods for eliminating the blistering and swelling problem.

## II. Future Work

Compilation of the data on slip-cast fused silica will be continued.

Efforts will be continued to determine the cause and methods of eliminating swelling and blistering in the Al-U<sub>3</sub>O<sub>8</sub> fuel plate. If the blistering and swelling cannot be eliminated, or if the results of the kinetics study appear likely to be compromised by the uncertainties concerning the nature of the sample, efforts will be begun to obtain a replacement fuel plate.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

U J. D. Walton, Jr., Head,  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA 30332

December 13, 1963

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 61, Project B-153 Covering  
the Period from 1 November 1963 to 1 December 1963  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Work

The supplementary survey of the literature on slip-cast fused silica was continued.

Attempts were continued to eliminate swelling in the new ATR fuel plates during x-ray testing. Vacuum annealing for one hour at 1100° F and for one hour at 1150° F was found to decrease the incidence of swelling to a tolerable level. Upon metallographic examination, however, some specimens showed much more reaction than was seen during similar treatment of specimens from the first plate.

In order to avoid any possible errors in the reaction kinetics resulting from contamination of the new plate, the decision was made to reject this material and proceed with a new dispersion. The new dispersion will be a reference ATR fuel plate from the Oak Ridge fabrication study. Use of this plate should completely eliminate any inconsistencies arising from material composition or fabrication variables. X-ray test specimens will be prepared by machining the cladding from one side of the fuel plate, leaving the meat exposed. The 20 mil thickness of fuel meat should be adequate for the test.

Evaluations of etching agents for reacted Al-U<sub>3</sub>O<sub>8</sub> dispersions were continued. A 0.5 per cent HF solution applied by 40 second swabbing was found to produce differential color staining of the phases in the reacted

material. Preliminary studies indicated that the colors produced are stable and reproducible. Efforts were begun to correlate the stain colors with phase identification by x-ray diffraction and electron microprobe analysis.

## II. Future Work

The supplementary literature survey for fused silica will be continued.

Evaluations of the etching agents for reacted  $\text{Al-U}_3\text{O}_8$  dispersions will be extended.

Upon receipt of the ATR plate, machining of the necessary x-ray specimens will be begun.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved: \_\_\_\_\_

J. D. Walton, Jr., Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA 30332

January 17, 1964

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 62, Project B-153 Covering  
the Period from 1 December 1963 to 1 January 1964  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Work

The supplementary survey of the literature on fused silica was continued.

Samples of typical foamed silica were obtained from Glasrock Products, Inc. A brief series of strength and porosity determinations was begun.

The reference ATR fuel plate was received on January 3 and machining was begun on January 6. The cladding was removed from one side of the fuel plate with little difficulty, leaving the fuel meat exposed. High temperature dynamic x-ray runs were begun to determine the Al-U<sub>3</sub>O<sub>8</sub> reaction rate. The residual cladding on the lower side of the test specimen was sufficiently fluid at a temperature of 1400° F to flow when the angle of inclination of the sample was changed. The fuel meat showed little or no tendency to flow with the result that the cladding flowed into a wedge below the meat, changing the x-ray angle of incidence. Since the x-ray system is of the usual fixed source type, this caused a complete loss of alignment.

Attempts were begun to eliminate the alignment changes by mechanical restraint of the specimen. If this proves unsuccessful, realignment of the system will be necessary after each x-ray sweep.


This will decrease the effective scanning speed of the system by approximately 50 per cent. Complete removal of the cladding from both sides of the specimen will be attempted as a last resort. This is expected to be unsuccessful, as a result of financial limitations, since great care will be required to preserve the extremely thin fuel meat.

## II. Future Work


The supplementary literature survey for fused silica will be continued.

Attempts to measure Al-U<sub>3</sub>O<sub>8</sub> reaction rates will be continued using dynamic x-ray diffraction and chemical and metallographic analysis.

Respectfully submitted,

 U. D. Fleming  
Senior Investigator

Approved:

 J. D. Walton, Jr., Head,  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA 30332

February 7, 1964

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 63, Project B-153 Covering  
the Period from 1 January 1964 to 1 February 1964  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Work

Compilation and coordination of data for the final report on slip-cast fused silica was continued.

Two reference fuel plates containing approximately 35 weight per cent  $U_3O_8$  were obtained from the Oak Ridge National Laboratory. The cladding was removed from one side of these plates to furnish an exposed Al- $U_3O_8$  surface for testing in the dynamic x-ray diffraction system. Initial attempts were made to follow the kinetics of the Al- $U_3O_8$  reaction in these specimens at temperatures up to 1800° F. The bottom layer of cladding on which the sample rested was sufficiently fluid at testing temperatures to flow when the x-ray diffraction table was tilted. This resulted in a loss of alignment of the sample and failure to obtain representative diffraction peaks for  $U_3O_8$  and  $UO_2$ .

In order to avoid the difficulties encountered from allowing the sample to rest on the residual backside cladding, a modification of the x-ray furnace was made so that the sample could be rested on the machined surface upon a stainless steel grid supported from alumina bars by Kanthal wires. The majority of the wires in the grid perpendicular to the direction of transmission of the x-ray beam were removed, leaving large openings in the grid parallel to the direction of x-ray transmission. In this manner, satisfactory diffracted beam intensity was maintained. Initial runs with this system orientation proved satisfactory. The fuel meat did not flow enough to interfere

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with either alignment or diffraction intensity. No reaction was noted between the fuel meat and the stainless steel after 7 runs using the same grid.

Dynamic x-ray runs were made up to a sample testing temperature of 2000° F. A rapid early loss of the  $U_3O_8$  diffraction peak was noted in all runs. This indicates an early conversion of the outside layer of the  $U_3O_8$  to  $UO_2$ , producing a  $UO_2$  layer thick enough to prevent penetration of the x-rays to the residual  $U_3O_8$  beneath. The thickness of this layer is estimated to be from 6 to 13 microns. On further heating, an early rapid reduction of  $UO_2$  was noted followed by a period during which reaction rate decreased considerably before complete reaction of the  $UO_2$ . With higher testing temperatures the initial rapid reaction of  $UO_2$  was increasingly difficult to follow. At 2000° F the initial rapid reduction period was completed by the time the second x-ray scan of the  $UO_2$  peak could be made.

Chemical analyses were begun using spot check samples in order to fix the x-ray diffraction rate curve on the composition axis. These analyses will be used to determine the extent of reaction during the development of the x-ray blocking layer of  $UO_2$  and during the period of initial rapid  $UO_2$  reduction. These analyses will disclose whether either reaction exceeds the allowable 3 per cent reaction during temperature equilibration which was previously agreed to be acceptable.

## II. Future Work

Compilation of the final report on slip-cast fused silica will be begun.

Dynamic x-ray diffraction and chemical analysis will be continued using the 35 per cent reference ATR Plates to determine the Al- $U_3O_8$  reaction kinetics.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved:

J. D. Walton, Jr., Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA 30332

March 15, 1964

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 64, Project B-153 Covering  
the Period from 1 February 1964 to 1 March 1964  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Work

Dynamic x-ray diffraction runs were made using ATR reference plate samples in the inverted system developed during the preceeding month. Survey scans were made up to the maximum temperature attainable in the x-ray furnace, 2100° F. Although the cladding melted and deformed, the exposed fuel meat was stable enough to avoid loss of the x-ray beam alignment. At 2100° F, the beam windows had limited service life, but a run could be completed before window failure.

Satisfactory x-ray traces were obtained up to approximately 1850° F. In these runs, the  $UO_2$  peaks grew to a maximum and then dropped. The initial growth period corresponded to a loss of  $U_3O_8$  diffraction peaks and indicated formation of a  $UO_2$  shell around the original  $U_3O_8$  particles. The subsequent loss of  $UO_2$  diffraction intensity represented conversion of  $UO_2$  to U-Al alloy phases with a concomitant decrease in  $UO_2$  volume fraction. The  $U_3O_8$  peaks could be followed only to approximately the point of maximum  $UO_2$  peak area, indicating that this point corresponded to formation of an extinction thickness of  $UO_2$ . Approximate x-ray absorption calculations indicated that this thickness should be of the order of 5-10 microns. The  $UO_2$  peak area at first decreased fairly rapidly after the peak was reached and then more slowly.

Above approximately 1850° F, the  $UO_2$  peak area passed its maximum before a single complete x-ray scan could be made about the  $UO_2$  diffraction

peak. In runs above approximately 1900° F, the initial rapid UO<sub>2</sub> decrease was complete before the first scan could be made. This indicated that the dynamic x-ray system is essentially incapable of following the reaction above 1850° F.

Chemical analyses were made using a few samples heated to the UO<sub>2</sub> maximum and cooled as rapidly as possible to determine the conversion prior to thermal equilibration. At approximately 1850° F, the conversion was equivalent to reduction of approximately seven per cent of the U<sub>3</sub>O<sub>8</sub> to U-Al alloy phases. Since this exceeded the three per cent equilibration conversion previously decided to be acceptable, 1850° F was greater than the maximum temperature at which the x-ray system could be relied upon to show the initial conversion kinetics.

An attempt was made to extrapolate the kinetics below 1850° F to 2100° F to predict the high temperature reaction rate. The lower temperature rates were plotted according to the Arrhenius criterion. The resulting relationship showed consistent increases in reaction rate with temperature but the curve showed a variation in log reaction rate vs. reciprocal temperature which was of much greater than first order. Extrapolation of this curve to 2100° F appeared foolhardy.


Attempts were begun to form some estimate of reaction rates at the higher temperatures by increasing the heating rate. This could not be done in the x-ray system since beam alignment is necessary prior to beginning the heating cycle. The method chosen was dropping the sample into a preheated argon atmosphere furnace followed by quenching in water after a set heating time. Efforts were begun to determine the maximum temperature increase rate in the sample in this system. A DTA furnace was modified for this purpose and heating rate runs were begun.

## II. Future Work

If the heating rates in the drop-and-quench system are found to be significantly higher than in the x-ray system, kinetics runs will be begun. Samples will be removed and quenched at pre-set times. The U<sub>3</sub>O<sub>8</sub> conversion will be determined from chemical analysis and metallography. As previously mentioned, this method will be subject to more statistical defects, if successful at all, than the dynamic x-ray technique. As a result, investigations of the reaction kinetics probably can be made only at one temperature with the time and funds available.

Respectfully submitted,

J. D. Fleming  
Senior Investigator

Approved: 

J. D. Walton, Jr., Head  
High Temperature Materials Branch

# GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA 30332

April 16, 1964

Reactor Division  
Oak Ridge Operations Office  
U. S. Atomic Energy Commission  
Post Office Box E  
Oak Ridge, Tennessee

Attention: Dr. David F. Cope, Director

Subject: Monthly Letter Report No. 65, Project B-153 Covering  
the Period from 1 March 1964 to 1 April 1964  
Contract No. AT-(40-1)-2483

Gentlemen:

## I. Experimental Work

Since the initial rate of the  $\text{Al-U}_3\text{O}_8$  reaction proved to be too rapid for determination with the dynamic x-ray system, studies were begun in which samples were heated rapidly in a modified DTA furnace and then subjected to post-heating chemical analysis. In these studies the sample was supported on a steel grid in the water-cooled observation port leading into the DTA furnace. The steel grid was held against the observation window by an external magnet. Aluminum foil was placed at the bottom of the observation tube to shield the sample from the interior of the furnace. The oxide film held the aluminum foil together although it was molten and the sample temperature did not exceed  $400^\circ\text{F}$  when the furnace temperature was held at  $2100^\circ\text{F}$ . When the furnace had equilibrated, the magnet was removed, allowing the sample to fall through the aluminum foil and into the furnace. After the sample had been heated for the desired time, the top of the furnace was removed and the fused silica hearth and sample were quenched. Water was used in the initial quenching studies but this was discarded when the samples showed sufficient oxidation to affect the results from the post-heating chemical analysis. Later quenching was in liquid nitrogen, which showed no tendency to react appreciably with the samples.

In order to provide a thermal history for the samples heated in the DTA furnace, a series of runs was made in which thermocouples were spot welded to samples which were then inserted into the furnace in a manner similar to that described above. The temperature of the samples during heating was recorded. These temperature profiles showed good reproducibility. Approximately

80 seconds was required to reach 2000° F.

After being heated, the samples were treated with a mixture of methyl alcohol, and iodine, which dissolves the aluminum alloy and the uranium-aluminum inter-metallic compounds resulting from the reaction. The reacted mixture was filtered and weighed. Following this weighing, the samples were oxidized at 900° F in air and another weighing was made. From these two weighings, material balances permit the determination of the amount of  $U_3O_8$  reduced to  $UO_2$  and the amount of  $U_3O_8$  reduced to uranium-aluminum intermetallic compounds. Since the weight change reflecting the reduction to  $UO_2$  is generally of the order of one milligram or less, and since a microgram balance was not available, this portion of the analysis was characterized by poor accuracy. Attempts are now being made to secure funds for the purchase of a microbalance. If such a balance can be obtained, the accuracy of the  $UO_2$  analysis will be substantially improved.

Using the procedure described above, Al- $U_3O_8$  samples were heated for periods of 60, 80, 100, and 120 seconds. The samples were subjected to chemical analysis using the methanol-iodine dissolution technique. The amount of  $U_3O_8$  reduced to uranium-aluminum intermetallics ranged from 6 to 14 per cent. The results showed a high degree of variability. Since statistical analysis will evidently be required, a series of runs was begun to provide sufficient data for this analysis.

Since in no case was an extent of reaction less than 6 per cent noted, the heating and quenching approach will obviously be unable to display the reaction kinetics below a total reaction of 3 per cent, the equilibration condition previously established for this work. Attempts were begun to provide a faster heating rate through the use of a plasma jet as the heating source. This approach will obviously involve many experimental difficulties and it is not anticipated that such a study can be completed within the remaining funds and time. An attempt will be made, however, to indicate the feasibility of this approach in case further work is desired.

## II. Future Work

Collection of sufficient data for statistical analysis will be continued using the heating and quenching method with the modified DTA furnace.

Efforts to demonstrate the plasma jet as a heating source will be continued.

Respectfully submitted,

*for* D. Fleming  
Senior Investigator

Approved:

*U* J. D. Walton, Jr. *U* Head  
High Temperature Materials Branch

QUARTERLY REPORT NO. 1

Project No. B-153

MATERIALS FOR  
HIGH TEMPERATURE NUCLEAR ENGINEERING APPLICATIONS

By

J. D. FLEMING, J. W. JOHNSON,  
PAUL BOLAND, S. H. BOMAR, and A. R. COLCORD

CONTRACT NO. AT-(40-1)-2483

U. S. ATOMIC ENERGY COMMISSION

15 AUGUST 1961 to 1 APRIL 1962



Engineering Experiment Station  
Georgia Institute of Technology

Atlanta, Georgia

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

QUARTERLY REPORT NO. 1

Project No. B-153

MATERIALS FOR  
HIGH TEMPERATURE NUCLEAR ENGINEERING APPLICATIONS

By

J. D. FLEMING, J. W. JOHNSON,  
PAUL BOLAND, S. H. BOMAR, and A. R. COLCORD

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CONTRACT NO. AT-(40-1)-2483

U. S. ATOMIC ENERGY COMMISSION

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15 AUGUST 1961 to 1 APRIL 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, Quarterly Reports were not submitted. Consequently, although this report is entitled Quarterly Report No. 1, several prior reports have been distributed. For a listing, see Section VII.

In order to distribute information as rapidly as possible, all work since the last major report, Progress Report No. 3, is included herein. Subsequent Quarterly Reports will cover only the appropriate calendar quarter.

This report covers the period from 15 August 1961 to 1 April 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 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 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.

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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  $U_3O_8$ . Since Al- $U_3O_8$  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 rate curves were run with fused silica samples cast using a graphite mold release. The devitrification rate was as low or lower than with any other mold release. This, together with its better handling characteristics, resulted in the graphite being used for all casting work with one piece molds. With multiple part molds, where release of the casting was not a problem, Keltex was used since it forms a strengthening film around the casting.

A further comparison was made of the ASTM C-20-46 water immersion test and the air displacement porosity system. The water test was capable of showing representative qualitative changes in the silica upon firing provided great care was exercised. The water test continued to be 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.

Further statistical analyses were made of the procedure for firing silica tensile test rings. These analyses showed a lack of sample uniformity, probably due to vertical temperature gradients in the furnace. A second order interaction indicated that the temperature gradients were not uniform from firing to firing.

A study was made of the crushing strength of slip cast fused silica. The crushing strength did not show a statistically significant dependence on sample height from 1/4 to 3-in. or on loading rate from 600 to 9000 pounds per minute. 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.

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.

Studies were made of the influence of mold vibration and pressure application on the casting rate of 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 cast 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.

Studies of the mixing characteristics of Al-U<sub>3</sub>O<sub>8</sub> powders showed that Baymal additions of approximately one per cent produced significant improvements in the ignition properties and fired structure.

The apparent theoretical density of the U<sub>3</sub>O<sub>8</sub> used was measured by air displacement and in a Beckman air pycnometer. The air displacement value was  $8.11 \pm 0.03$  gm/cc and the air pycnometer value was  $8.16 \pm 0.01$  gm/cc.

Tests with Al-U<sub>3</sub>O<sub>8</sub> thermets compounded with different aluminum contents showed that the ignition temperature decreased with increasing aluminum content. At 10 w/o aluminum, ignition occurred at 1640° F while indications were obtained of complete reaction of a 59.7 w/o aluminum thermet as low as 1200° F. With increasing aluminum content, the ignition became much less violent and the temperature excursion during ignition decreased markedly.

Chemical analyses indicated 95 per cent reaction of the aluminum in 14.6 w/o aluminum thermets and implied complete U<sub>3</sub>O<sub>8</sub> reaction in 35.7 and 59.7 w/o aluminum thermets.

X-ray diffraction analysis produced completely resolved traces for 14.6 and 59.7 w/o aluminum thermets. The 14.6 w/o thermets contained  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{UO}_2$ ,  $\text{UAl}_2$ , and  $\text{UAl}_3$ . Some residual  $\text{U}_3\text{O}_8$  was seen in samples compounded with  $\text{U}_3\text{O}_8$  of a particle size greater than 140 mesh. The relative amount of  $\text{UAl}_3$  increased with decreasing  $\text{U}_3\text{O}_8$  particle size. The 59.7 w/o samples contained  $\alpha\text{-Al}_2\text{O}_3$  and  $\text{UAl}_4$ . In some cases,  $\text{UAl}_2$ ,  $\text{UAl}_3$ ,  $\text{UO}_2$ , and residual  $\text{U}_3\text{O}_8$  were observed.

Initial electron microprobe analyses were made of fired  $\text{Al-U}_3\text{O}_8$  thermets. These analyses showed the presence of  $\text{UO}_2$ ,  $\text{UAl}_2$ , and  $\text{Al}_2\text{O}_3$ .

$\text{Be-U}_3\text{O}_8$  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  $\text{Al-U}_3\text{O}_8$  reactions.



### III. EXPERIMENTAL WORK

#### A. Slip Cast Fused Silica

##### 1. Graphite Mold Release

Devitrification rate studies were made at 2200° F in the high temperature x-ray diffraction system using samples cast into U. S. Gypsum No. 1 plaster with the graphite mold release<sup>1</sup>. Even though the samples were fired with the graphite in place, the devitrification rate was uniformly lower than with samples cast with Keltex and fired after removal of the Keltex as in shown in Figure 1. Mold contaminants held on the surface of the graphite were apparently removed by the burning off of the graphite instead of being fixed by the silica as was the case with Keltex.

The graphite release agent proved superior for use in one piece bar molds since, as opposed to Keltex, there was no tendency to roll up on the casting surface and prevent removal of the casting. As a result of this and the low devitrification rate, the graphite release was adopted for all casting work in one piece molds. With multiple piece molds, where binding is not a problem, the Keltex is advantageous since it imparts slightly better green strength by surrounding the casting with a film.

##### 2. Porosity

##### a. Further Comparison of Air Displacement and Water Displacement Tests

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 reported in Progress Report No. 3 indicated that the qualitative

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<sup>1</sup>Progress Report No. 2, p. 13.

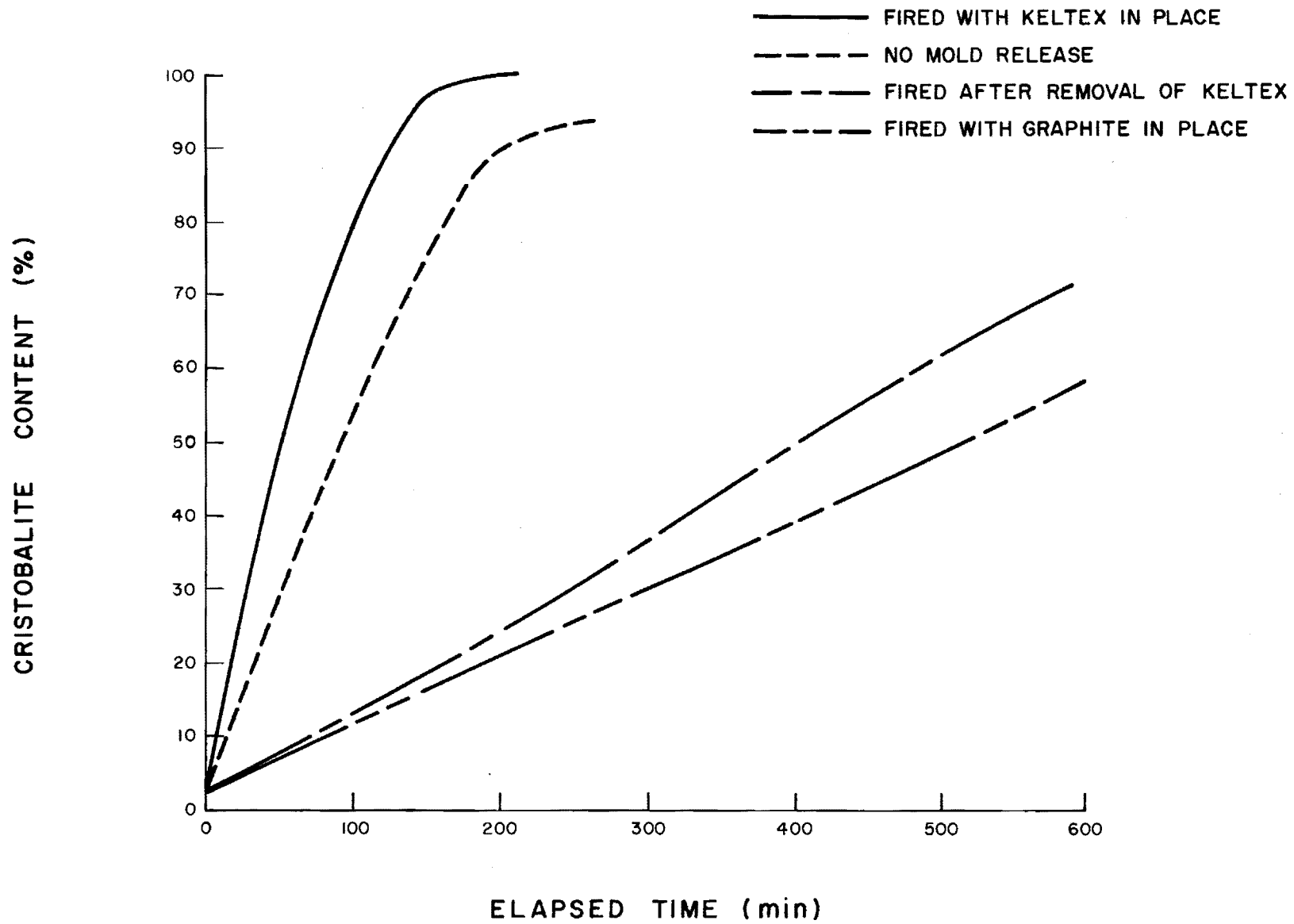


Figure 1. Extent of Devitrification with Different Mold Release  
2200°F Firing Temperature.

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-in. in diameter by 5-5/8-in. long, were fired at 2200° F for 2, 4, 8, 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 2<sup>1</sup>. 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 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.

#### b. Correction of Firing Time

The firing procedure which has been followed to date is:

1. The furnace is pre-heated to the firing temperature.

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<sup>1</sup>The porosity of the unfired bars could not be determined by water displacement since the green structure could not withstand boiling.

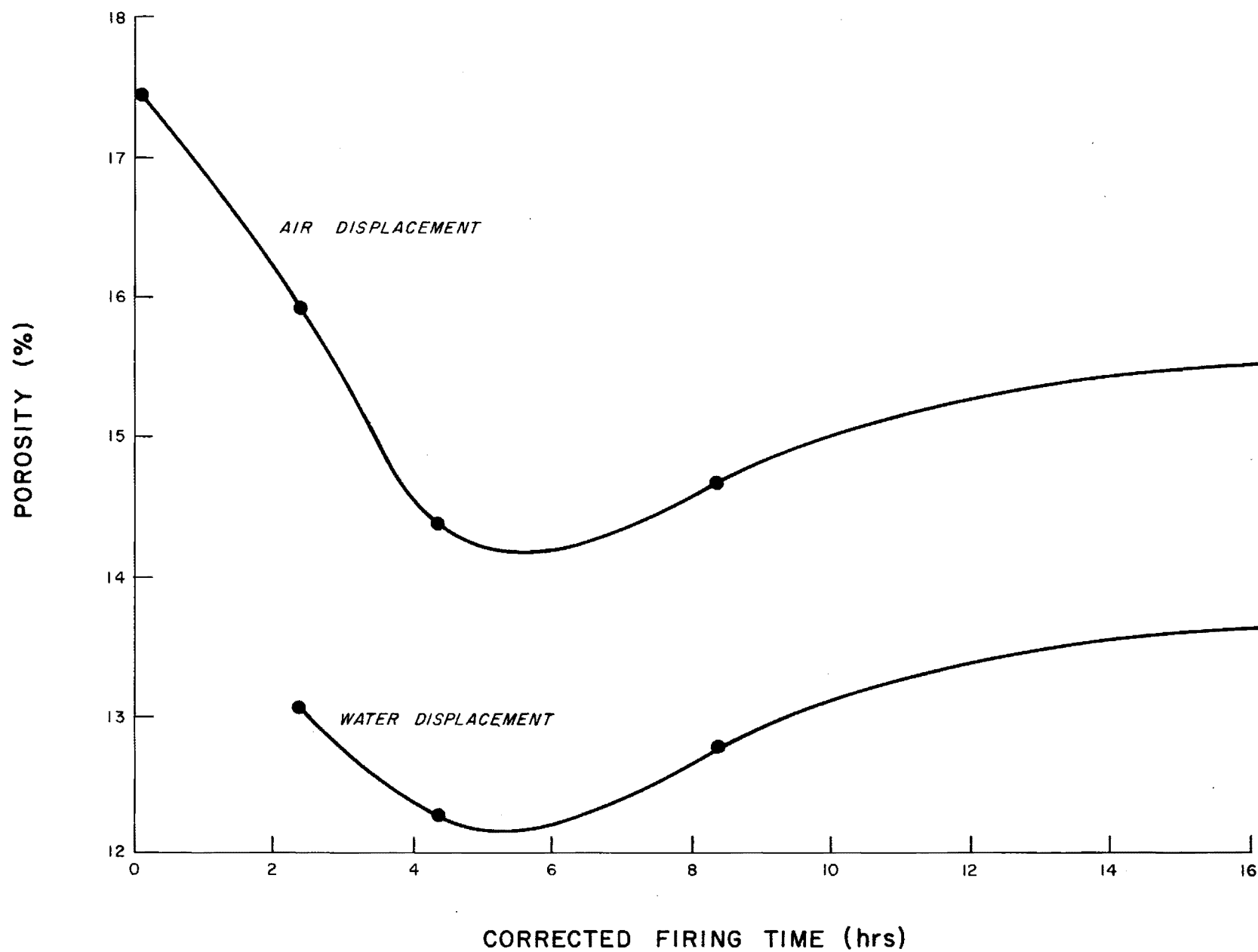


Figure 2 . Porosity Profiles at 2200°F From Water Displacement and Air Displacement.

2. The samples are inserted. During this step, the furnace temperature drops considerably.
3. The furnace is reheated to the firing temperature at full power.
4. The time at which the furnace again reached the firing temperature is set as the base line for the firing time  $\theta_u$ . This is the correlating parameter which has been used in the past.

Use of the firing time defined above as a correlating parameter is obviously a poor choice since the samples would undergo significant changes during the heat-up period. The magnitude of these changes was determined by making a series of zero-time firings, i.e. removing and water quenching the bars at the instant the furnace returned to the set firing temperature. The density characteristics of these zero-time samples are compared with dried but unfired samples in Table I. A t test showed a porosity of 17.26 or lower to be significantly different at the 95 per cent level from the unfired porosity of 17.44. This indicated the need for a heat-up time correction for firings at 2100° F or above.

In principle, any property of the fired bars could be used to establish a zero-time correction. In practice, however, the strengths suffered from a much greater lack of reproducibility than the void volume properties. The porosity could not be plotted to yield a straight line and extrapolation along the curved lines could not be carried out with any degree of reliability. The theoretical density showed too small a change to be useful for extrapolation. The only suitable property proved to be the bulk density which was correlated reasonably well by the equation

$$B = a + b \log (\theta_u + 1) \quad 1)$$

TABLE I  
COMPARISON OF ZERO-FIRED AND UNFIRED SLIP CAST SILICA

<u>Firing Temperature</u> (°F)	<u>Time for Reheat</u> (hr)	<u>Porosity*</u> (%)	<u>Bulk Density*</u> (gm/cc)	<u>Apparent* Theoretical Density</u> (gm/cc)
Unfired		17.44 ± 0.11	1.856 ± 0.005	2.248 ± 0.006
2000	0.23	17.44 ± 0.11	1.863 ± 0.003	2.256 ± 0.002
2100	0.32	17.21 ± 0.17	1.860 ± 0.003	2.246 ± 0.006
2133	0.35	17.22 ± 0.13	1.864 ± 0.003	2.252 ± 0.003
2166	0.37	16.96 ± 0.24	1.868 ± 0.003	2.250 ± 0.006
2200	0.38	16.64 ± 0.15	1.869 ± 0.003	2.242 ± 0.002
2300	0.79	14.89 ± 0.19	1.906 ± 0.005	2.239 ± 0.003

\* Ranges shown are  $\pm 2.09 s_m$  where  $s_m$  is the standard deviation of the mean. This is the range which should contain the average value cited within 95 per cent confidence.

where B is the bulk density,  $\theta_u$  is the uncorrected firing time, and a and b are constants. Equation 1 was fitted to the data for each firing temperature by the least squares technique and the resulting equations were extrapolated to the unfired density to obtain a firing time correction for each temperature. While this procedure gave reasonable results for the correction time, just as efficient correlation of the data was afforded by a modified form of Equation 1.

$$B = 1.856 + b' \log (\theta + 1) \quad 2)$$

where

$$\theta = \text{corrected firing time} = \theta_u + \theta_R$$

$\theta_u$  = time following point at which furnace returns to firing temperature

$\theta_R$  = reheat time from Table I.

The values of  $b'$  calculated by least absolute deviations are given in Table II. The calculated equations and data are plotted in Figure 3. Since this correlation procedure was more direct and just as satisfactory, the reheat time, rather than the extrapolated correction time, was chosen to normalize the uncorrected firing times.

TABLE II  
SLOPE OF BULK DENSITY EQUATION

<u>Temperature</u>	<u><math>\theta_R</math></u>	<u><math>b'</math></u>
2000	0.23	0.013
2100	0.32	0.038
2133	0.35	0.052
2166	0.37	0.075
2200	0.38	0.093
2300	0.79	0.202

NOTE: The shaded area associated with a given point represents the region which is expected to contain that point with 95 per cent confidence.

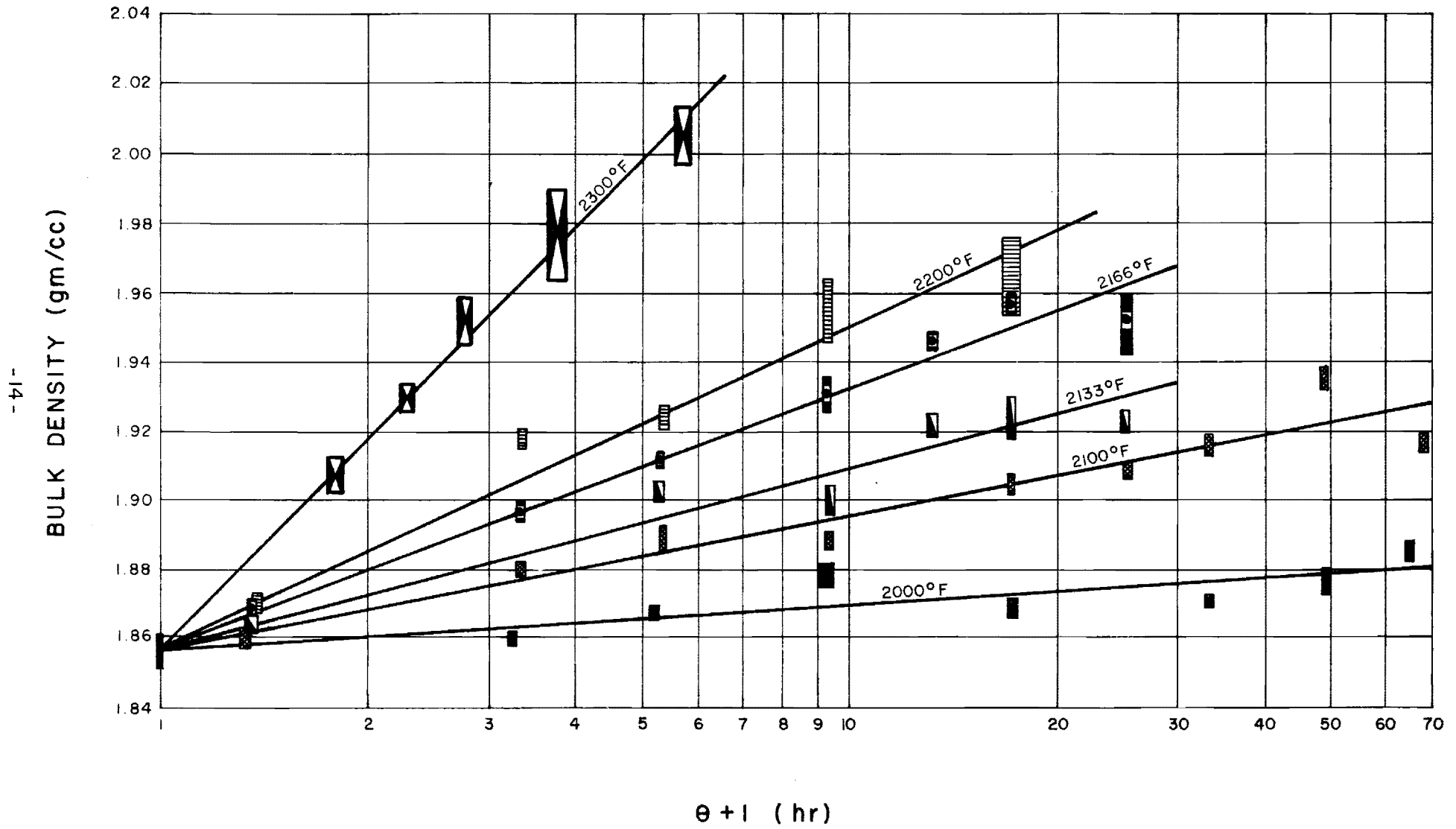


Figure 3. Bulk Density of Slip Cast Fused Silica as a Function of the Corrected Firing Time.



The real significance of this firing time correction is far from certain. The bulk density data could not be correlated with the power time functions characteristic of bulk diffusion controlled processes, indicating as previously proposed, that sintering in slip cast fused silica is a complex process related both to bulk diffusion and to devitrification. Equation 1 is probably not truly representative of the basic sintering mechanism and the derived firing time corrections probably have no theoretical meaning. This is particularly true since Equations 1 and 2 correlated the data equally as well. This would indicate that the correlation is insensitive to the correction time used and that the success of the correlation cannot be taken to imply fundamental significance. Since they do serve as effective correlating parameters, however, and do not dispute experimental observations, these corrections were used in all the correlations concerning slip cast fused silica given in this report unless otherwise noted.

c. Porosity and Density of Slip Cast Fused Silica

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 3 and 4.

The minimum porosity values in Figure 4 were obtained using four point Lagrangian interpolation. The time at which the minimum porosity is reached can be correlated by the equation

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

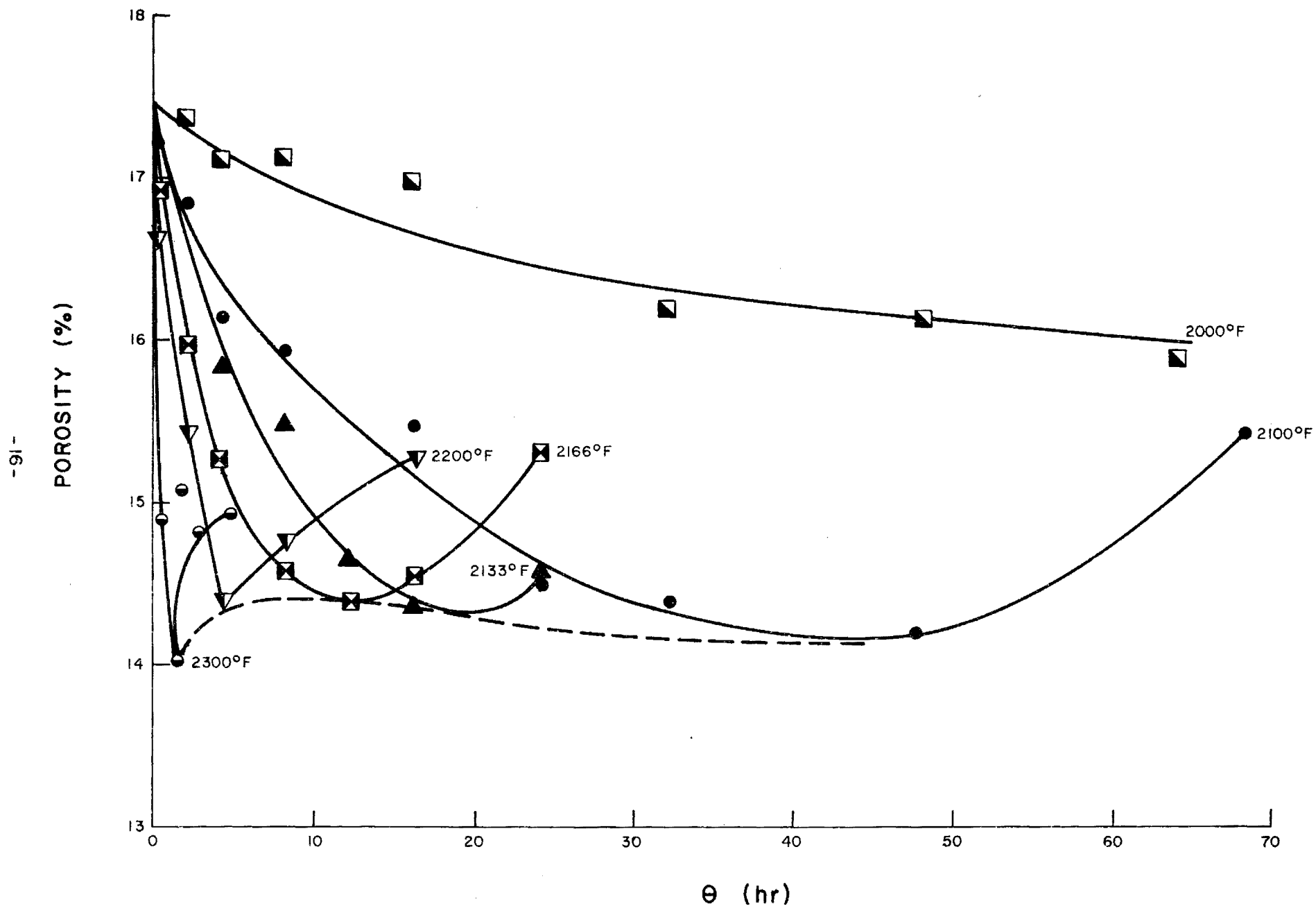


Figure 4. Porosity of Slip Cast Fused Silica as a Function of the Corrected Firing Time.

where

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

T = firing temperature, °F.

This equation, obtained by applying least squares to the interpolated data, is shown in Figure 5.

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

$$\theta_r = \frac{\theta}{\theta_m} . \quad 4)$$

The porosity is shown as a function of reduced firing time in Figure 6.

### 3. 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. 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 7.

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,

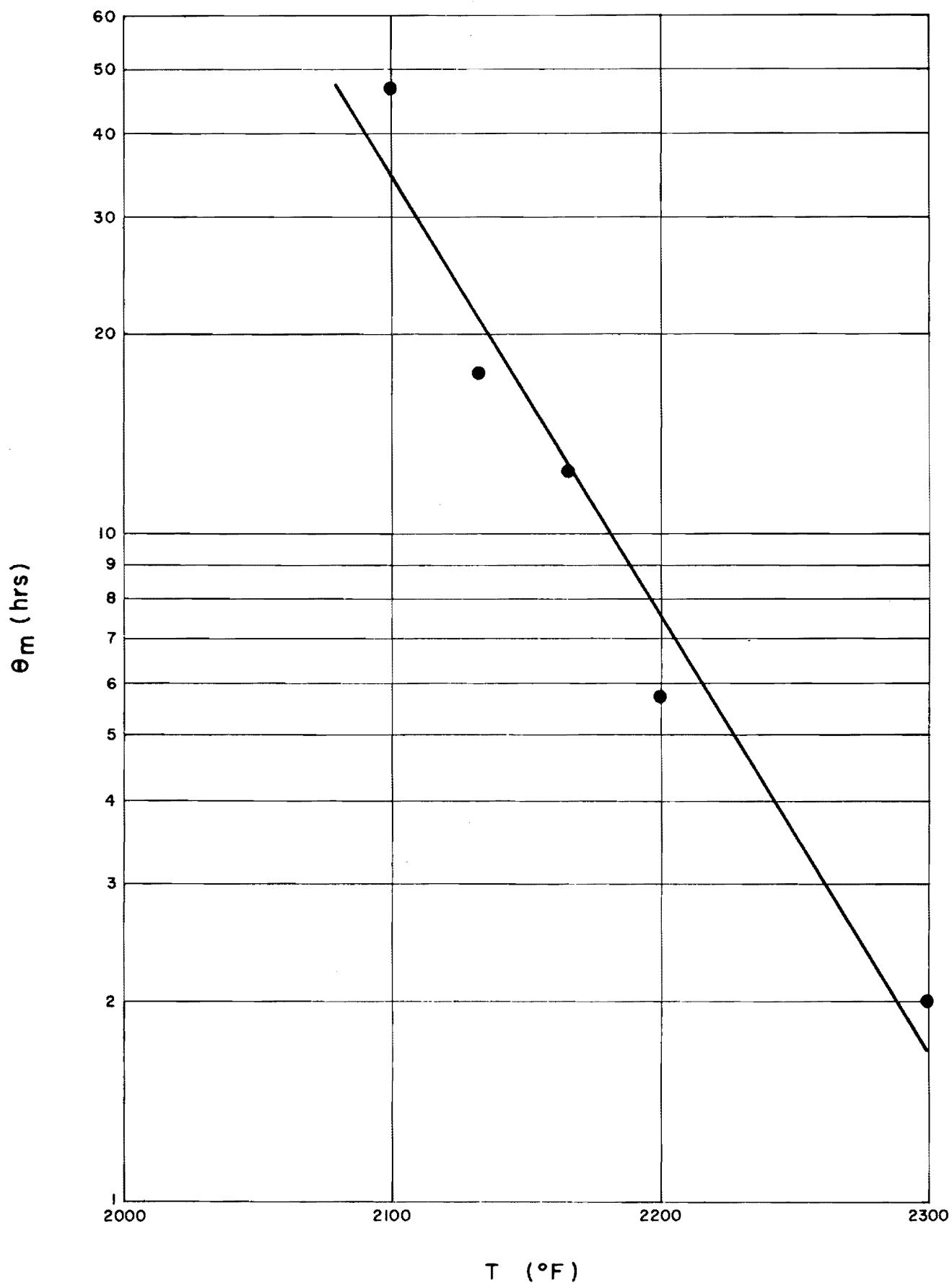


Figure 5. Corrected Time to Reach Minimum Porosity as a Function of Firing Temperature.

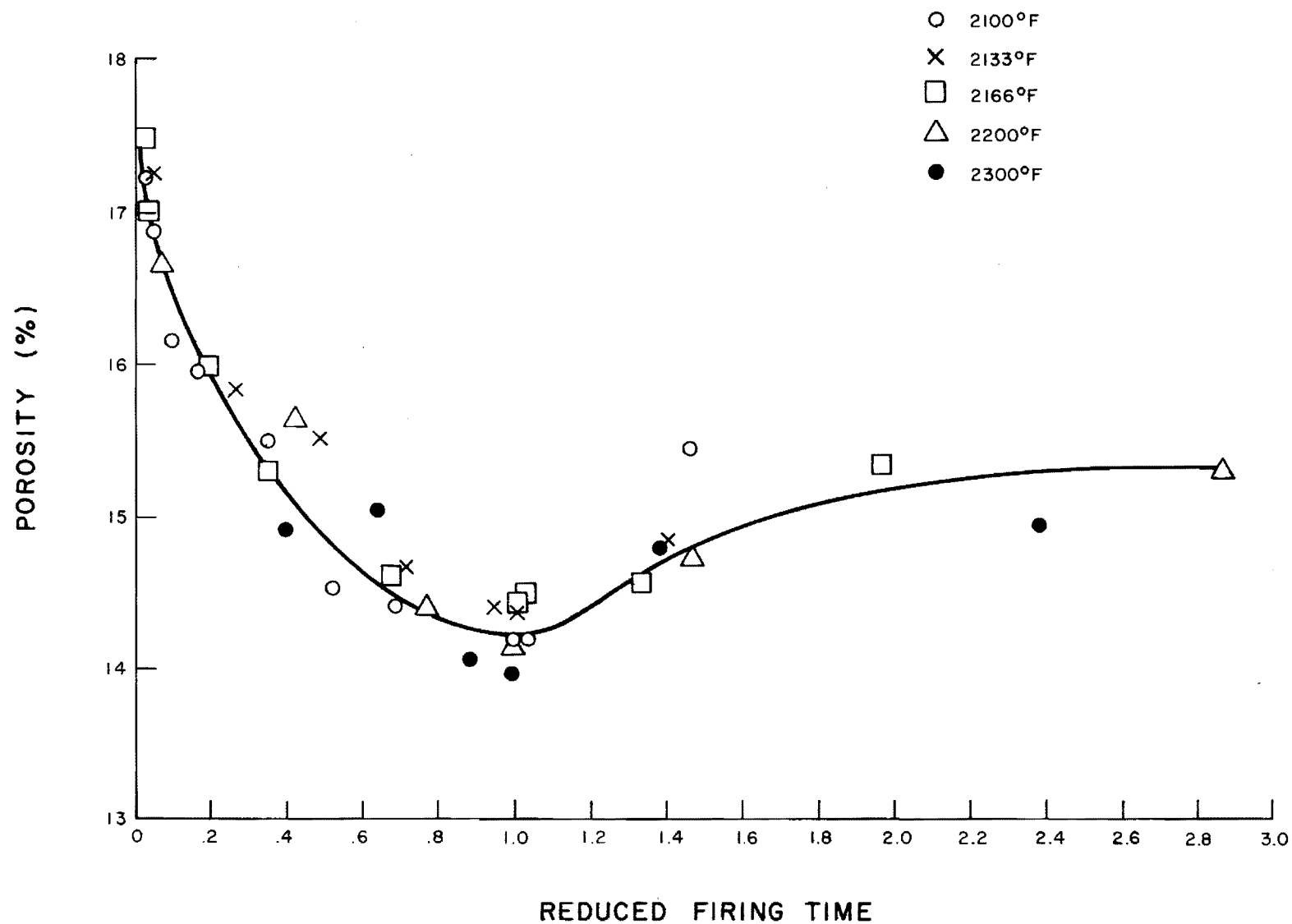


Figure 6 . Porosity as a Function of Reduced Firing Time.

NOTE:  $\theta_c$  IS THE CORRECTED FIRING TIME

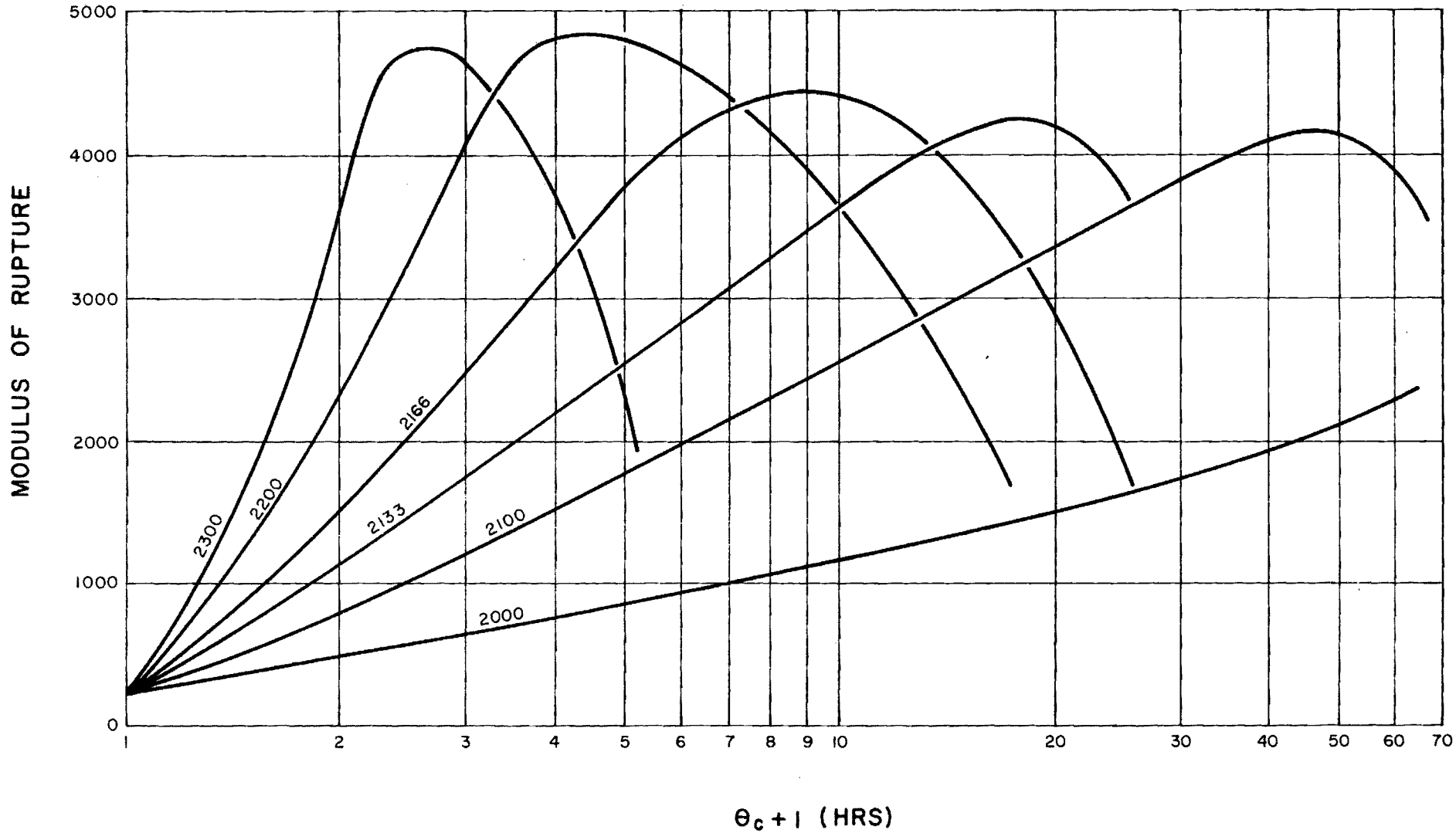


Figure 7. Modulus of Rupture as a Function of Firing Conditions.

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 7 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 6, 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.

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 temperatures 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

<u>Firing Temperature</u> (°F)	<u>Corrected Time For</u>	
	<u>Maximum Strength</u> (hr.)	<u>Minimum Porosity</u> (hr.)
2100	49.0	46.7
2133	19.0	17.4
2166	8.5	12.4
2200	3.3	5.7
2300	1.6	2.0

#### 4. Ring Tests

Further efforts were made to improve the reliability of the tensile data for slip cast fused silica. Since the major data scatter seemed to arise from the firing procedure, a more extensive series of firings was made with the rings separated by alumina tripod spacers in an attempt to reduce sample temperature differences. Five firings were made, each consisting of six stacks



of four rings. The rings were numbered so that the stack location and position in the stack could be determined. The rings were tested on a Tinius-Olsen universal tester and the data were analyzed.

A two factor analysis of variance was carried out in which the data were treated as five firings of 24 samples without replication. The results of this analysis are summarized in Table IV.

TABLE IV  
VARIANCE ANALYSIS OF FIRING AND SAMPLES

<u>Source</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F Ratio</u>
Firing	4	11,437	1.27
Sample	23	10,208	1.13
Error	92	9,006	
Total	119		

The results of Table IV show that neither the "firing" factor nor the "sample" factor are statistically significant; therefore the mean squares due to these factors become independent estimates of the experimental error variance. The failure of this analysis to detect any significant factors is probably due to the high experimental error and to the limited analysis design. For this reason two further statistical analyses were carried out with the same data. The first served to clarify the approach to the second, more comprehensive approach.

A two factor analysis of variance was made in which the five firings were considered replicates of samples at a particular level within a particular stack. The results of this analysis are given in Table V.

TABLE V  
VARIANCE ANALYSIS OF SAMPLE POSITION

<u>Source</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F Ratio</u>
Level within stack (L)	3	33,210	3.65**
Position of stack (S)	5	3,150	0.346
LXS Interaction	15	7,961	0.874
Error	96	9,107	
Total	119		

\*\* Significant at greater than the 97.5 per cent level of confidence.

The results of Table V show that the position of a particular sample within the stack, i.e. level within the stack, is a highly significant source of variation. On the other hand, the position of the stack and the combined effects of stack position and level are not significant. This indicates that the important variations in the furnace occur in the vertical direction.

A three factor analysis of variance was finally carried out to distinguish as far as possible the specific source of the variation. The three factors were the firing, the level within the stack, and the row in which the stack was positioned, i.e. the front row of three stacks or the back row of three stacks.

The three rings at a given level in a particular row were considered to be replicates. The primary results are summarized in Table VI.

TABLE VI  
VARIANCE ANALYSIS OF FIRING AND POSITION, THREE FACTOR

<u>Source</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F Ratio</u>
Firing (F)	4	11,437	1.743
Level (L)	3	30,643	4.68****
Row (R)	1	12,343	1.88
FXL Interaction	12	25,143	3.84****
FXR Interaction	4	5,144	0.785
LXR Interaction	3	9,505	1.46
FXLXR Interaction	12	6,950	1.06
Error	80	6,560	
Total	119		

\*\*\*\* Significant at greater than the 99.5 per cent confidence level.

Since the row does not appear as a significant single factor or in a significant interaction, the primary results of Table VI can be simplified by pooling non-significant terms. These results are given in Table VII.

TABLE VII

VARIANCE ANALYSIS OF FIRING AND POSITION, TWO FACTOR DEGENERATE

<u>Source</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F Ratio</u>
Firing (F)	4	11,437	1.706
Level (L)	3	30,643	4.58****
FXL	12	25,143	3.76****
Error	100	6,697	
Total	119		

\*\*\*\* Significant at greater than the 99.5 per cent confidence level.

The results in Table VII show the level within the stack to produce a significant variation in the tensile data and that the extent of this influence is not constant with different firings. This probably is a result of thermal gradients within the furnace and an inability to load the furnace, close the loading platform, etc. in a reproducible enough manner to produce the same thermal gradient from firing to firing.

The nature of the sources of variation in the ring firings is unfortunate in that the only course of action likely to improve the tensile data with a small experiment is a complete redesign of the furnace. In view of the prohibitive expense of this step, the only solution appears to be an increase in the number of samples tested under a particular set of conditions and a corresponding reduction in the number of conditions which can be studied.

5. Crushing Strength

a. Influence of Testing Conditions

Sets of silica cylinders of various lengths from 1/4 to 3-in. were cut from 3/4-in. diameter bars which were fired at 2200° F for an uncorrected time of 8 hours. The samples were crushed on a Tinius-Olsen Super L universal tester using cardboard spacers between the cylinder ends to act as alignment cushions. A loading rate of 2,400 pounds per minute was used. The results of this test are summarized in Table VIII.

TABLE VIII  
EFFECT OF SAMPLE LENGTH ON CRUSHING STRENGTH

<u>Sample Length</u> (in.)	<u>Crushing Strength</u> (psi)	<u>Standard Deviation</u> (psi)
1/4	23,040 $\pm$ 3,900 <sup>1</sup>	4,680
1/2	15,990 $\pm$ 2,480 <sup>1</sup>	2,970
3/4	18,010 $\pm$ 3,310 <sup>1</sup>	3,950
1	18,950 $\pm$ 5,790 <sup>2</sup>	4,660
2	19,830 $\pm$ 6,020 <sup>2</sup>	4,820
3	19,440 $\pm$ 6,130 <sup>2</sup>	4,910

1. Range shown is  $\pm 2.36 s_m$  where  $s_m$  is the standard deviation of the mean. This range should contain the mean within a 95 per cent confidence level.
2. Range shown is  $\pm 2.78 s_m$ . This range should contain the mean within a 95 per cent confidence level.

Quarterly Report No. 1, Project No. B-153

An analysis of variance was made using the data of Table VIII. This analysis failed to show a significant difference between the means at greater than the 90 per cent confidence level. In view of this and convenience of handling, a one inch sample size was selected as standard.

Following selection of the standard sample size, an investigation was made of the influence of loading rate on the crushing strength. One inch long cylinders were cut from 3/4-inch diameter bars fired at 2200° F for an uncorrected time of 8 hours. These samples were tested at loading rates of 600 to 9,000 pounds per minute on a Tinius-Olsen Super L universal tester. The results of this test are summarized in Table IX.

TABLE IX  
EFFECT OF LOADING RATE ON CRUSHING STRENGTH

<u>Loading Rate</u> (pounds/minute)	<u>Crushing Strength</u> <sup>*</sup> (psi)	<u>Standard Deviation</u> (psi)
600	20,820 $\pm$ 4,270	5,110
2,400	18,810 $\pm$ 4,890	5,860
4,800	19,820 $\pm$ 4,720	5,650
9,000	23,020 $\pm$ 5,130	6,140

\*Range shown is  $\pm 2.36 s_m$  where  $s_m$  is the standard deviation of the mean. This range should contain the mean within a 95 per cent confidence level.

The data of Table IX were subjected to an analysis of variance which failed to show a significant difference between the averages at greater than the 50 per cent confidence level. Since loading rate showed no influence on the crushing strength, 4,800 pounds per minute was selected as the standard rate inasmuch as it provided a convenient breaking time.

b. Crushing Strength of Slip Cast Fused Silica

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, crushing strengths, and ratios of the two strengths are tabulated in Table X.

The crushing strength and modulus of rupture tests differ in their sensitivity to structural flaws as is readily apparent from Figure 8 which shows the strength profiles for the 2200° F firings. 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

TABLE X  
CRUSHING STRENGTHS AND MODULI OF RUPTURE  
OF SLIP CAST FUSED SILICA

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



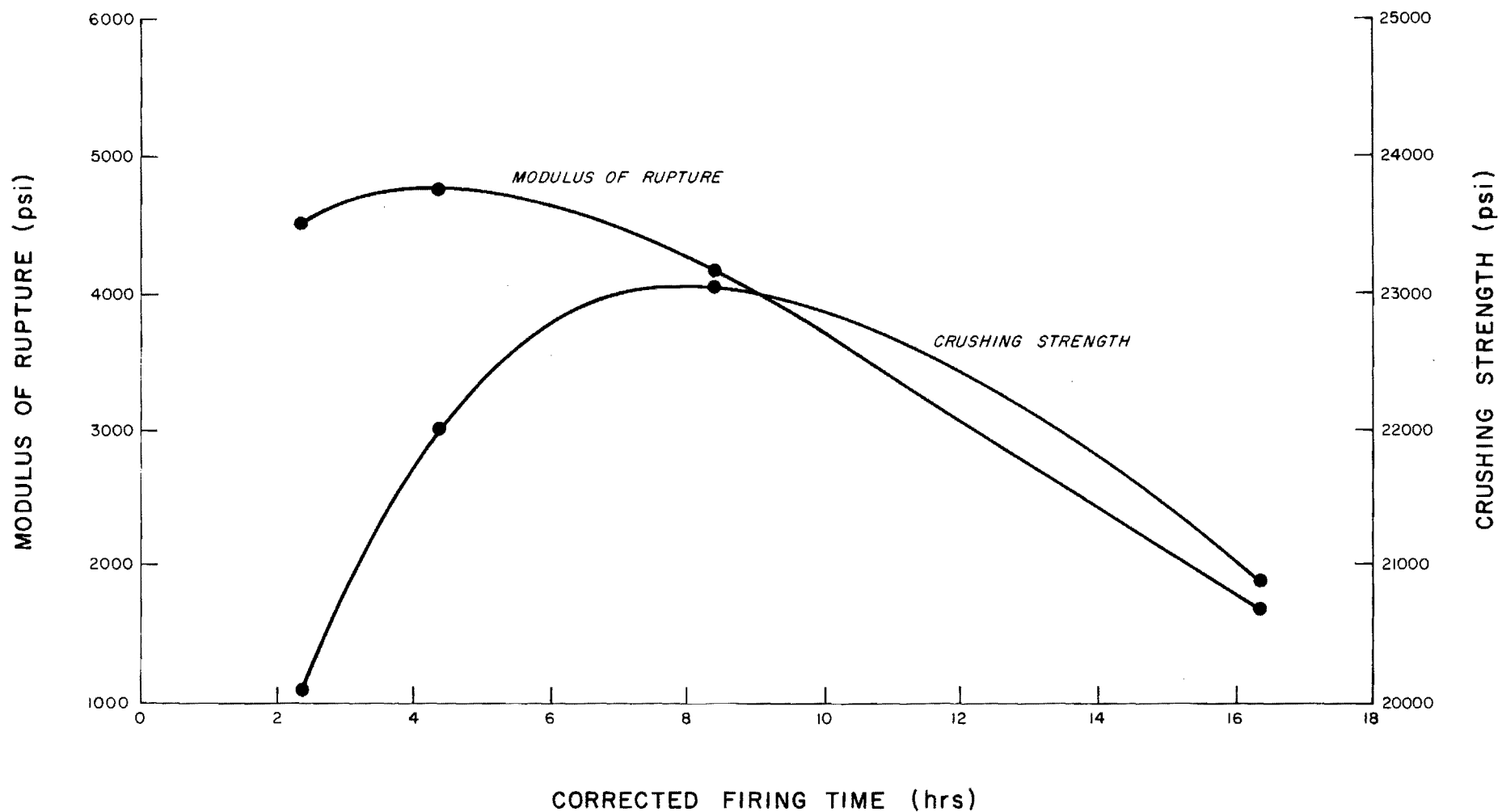


Figure 8. Modulus of Rupture and Crushing Strength Profiles for Slip Cast Fused Silica Fired at 2200°F.

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 crushing strength. This same trend is reflected in the ratio of crushing 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.

#### 6. 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 firing in steam, argon, and air. Sets of twelve 3/4-in. diameter by 5-5/8-in. long silica bars were cast in one piece molds using the graphite mold release. Sets were fired in a tube furnace under the following conditions:

1. Air was passed through the tube at 2.5 cu. ft. per hour, STP.  
Sets were fired for uncorrected times of 2, 4, 8, and 16 hours.
2. Saturated steam at 3.5 in. water absolute was passed through the tube at approximately 17 cu. ft. per hour, STP. Sets were fired for uncorrected times of 2, 4, and 8 hours.
3. The tube was evacuated and backfilled with argon twice. Argon was then passed through the tube at approximately 7 cu. ft. per hour, STP. Sets were fired for uncorrected times of 2, 4, 8, and 16 hours.

All firings were made at a furnace temperature of 2200° F. Since provisions were not available for introducing a thermocouple into the tube, the true firing temperature of the samples is unknown. This temperature should be lower than 2200° F as a result of the cooling effects of the flowing gases. A comparison of the air firings with normal firings in stagnant air indicated that the true firing temperature was probably quite close to 2200° F.

The porosity, bulk density, and apparent theoretical density of the samples were determined by air displacement. Following these measurements, the moduli of rupture were determined in three point loading by breaking each sample three times, once on a four inch span and, using the pieces from the first break, twice on a two inch span. The samples were then crushed and subjected to x-ray diffraction for cristobalite analysis.

In correlating the results of the firing atmosphere studies, no attempt was made to determine a correction time as described in Appendix A for the other silica firings. Such determinations will be made for future firings.

The porosities, bulk densities, moduli of rupture, and cristobalite contents of the samples are shown as functions of the uncorrected firing time in Figures 9 through 12<sup>1</sup>. The apparent theoretical densities are shown as a function of cristobalite content in Figure 13.

The most striking effect noted in this study was the strong influence of steam on the bulk diffusion<sup>2</sup> rate of the silica. The data of Figure 10 fitted by the method of averages, show that the bulk density is greatly

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<sup>1</sup>The cristobalite analyses of approximately 1 per cent approach the sensitivity limit of the x-ray technique and were not used in the correlation. These values could easily be in error by a factor of two.

<sup>2</sup>Bulk diffusion is used here only to represent a diffusion mechanism different from devitrification induced diffusion. The actual process might be viscous flow, surface diffusion, etc.

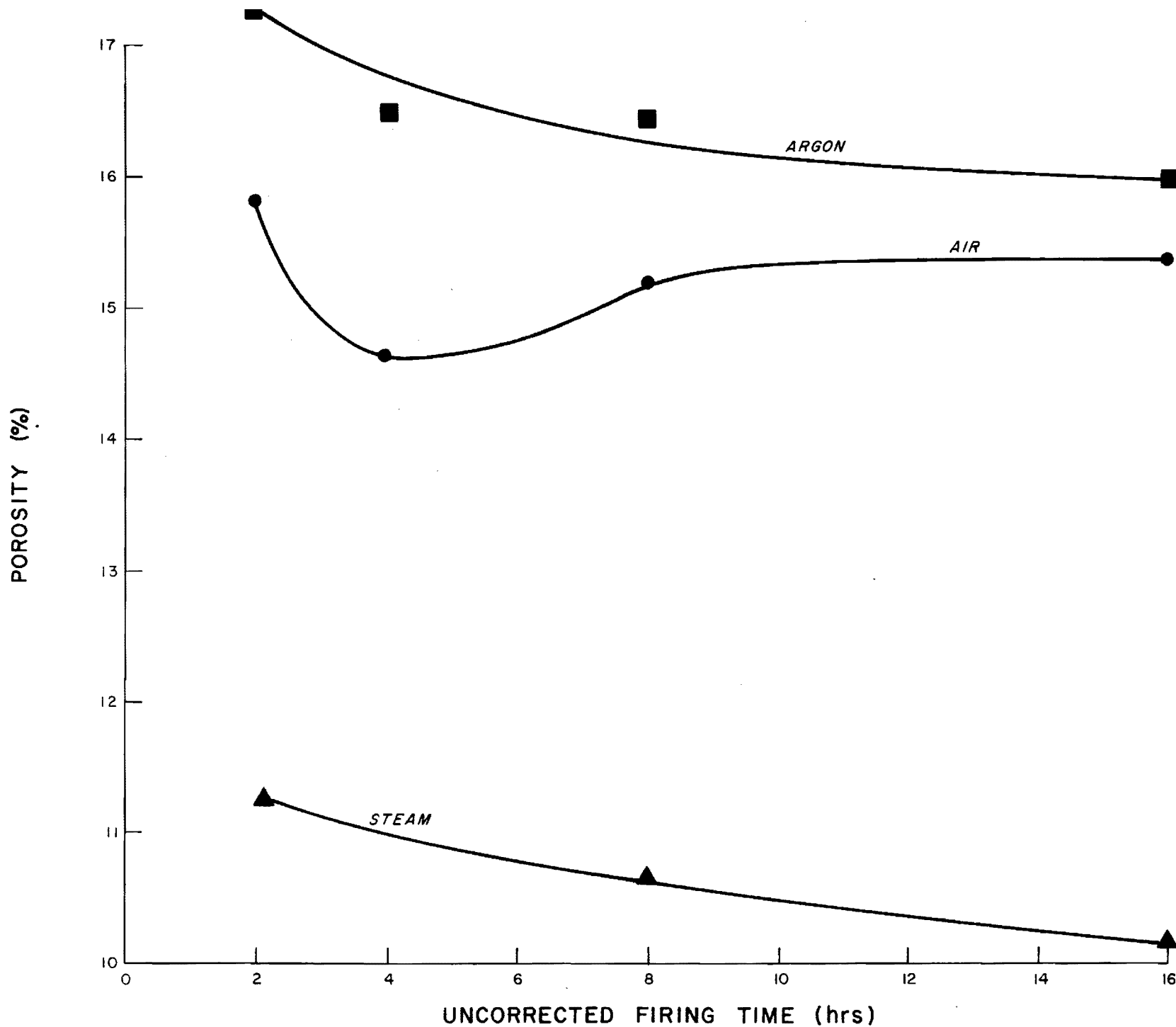


Figure 9 . Porosity of Slip Cast Fused Silica as a Function of Firing Atmosphere.

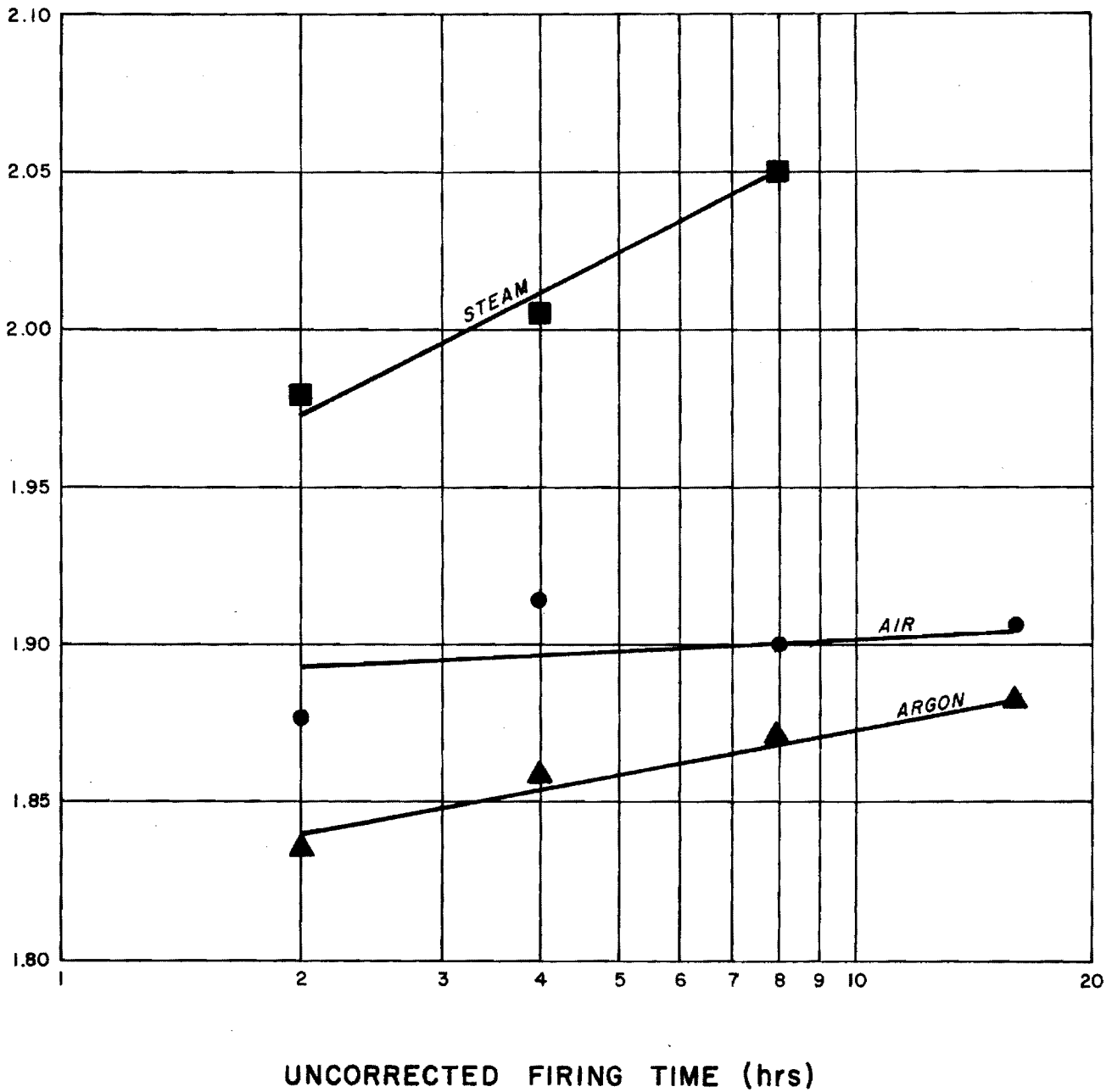


Figure 10 . Bulk Density of Slip Cast Fused Silica as a Function of Firing Atmosphere.

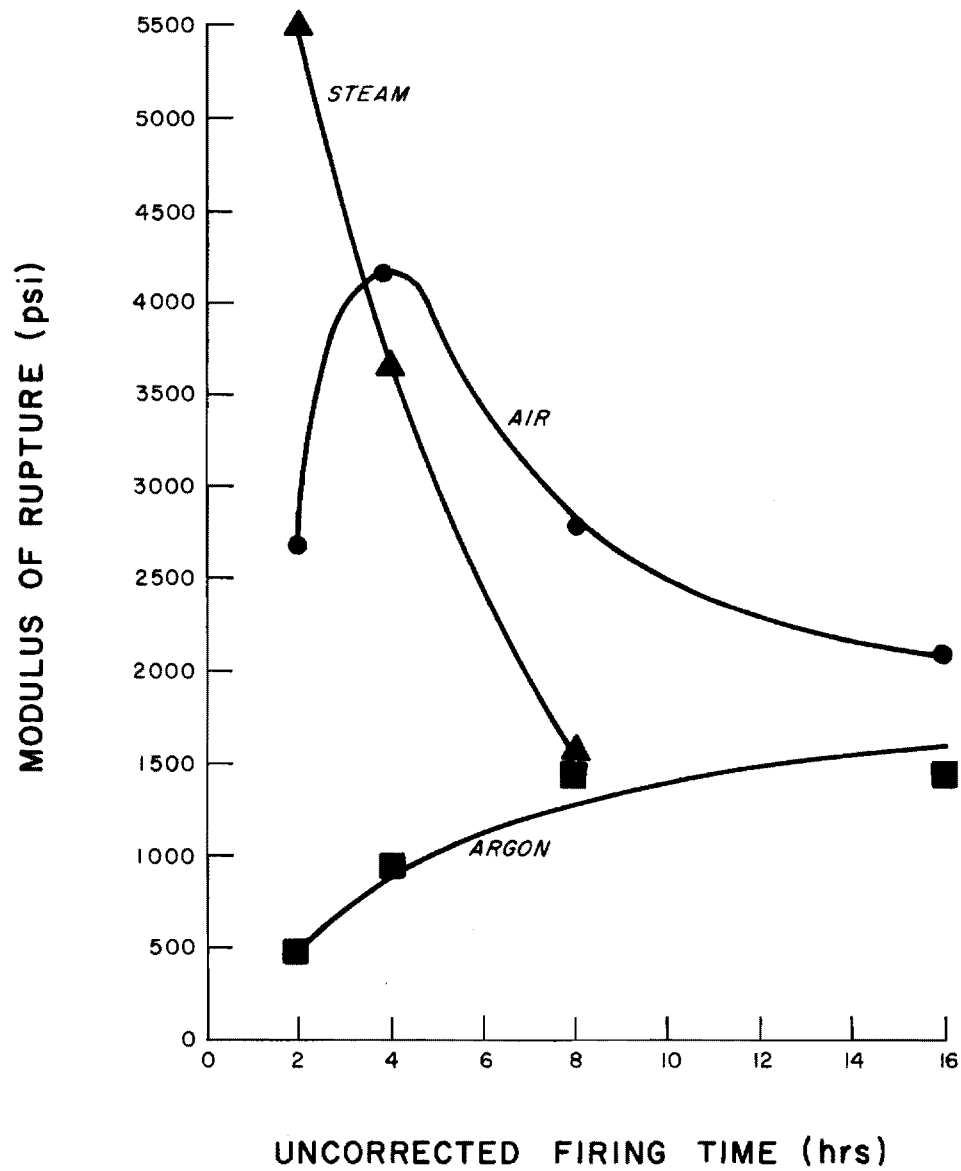


Figure II. Modulus of Rupture of Slip Cast Fused Silica as a Function of Firing Atmosphere.

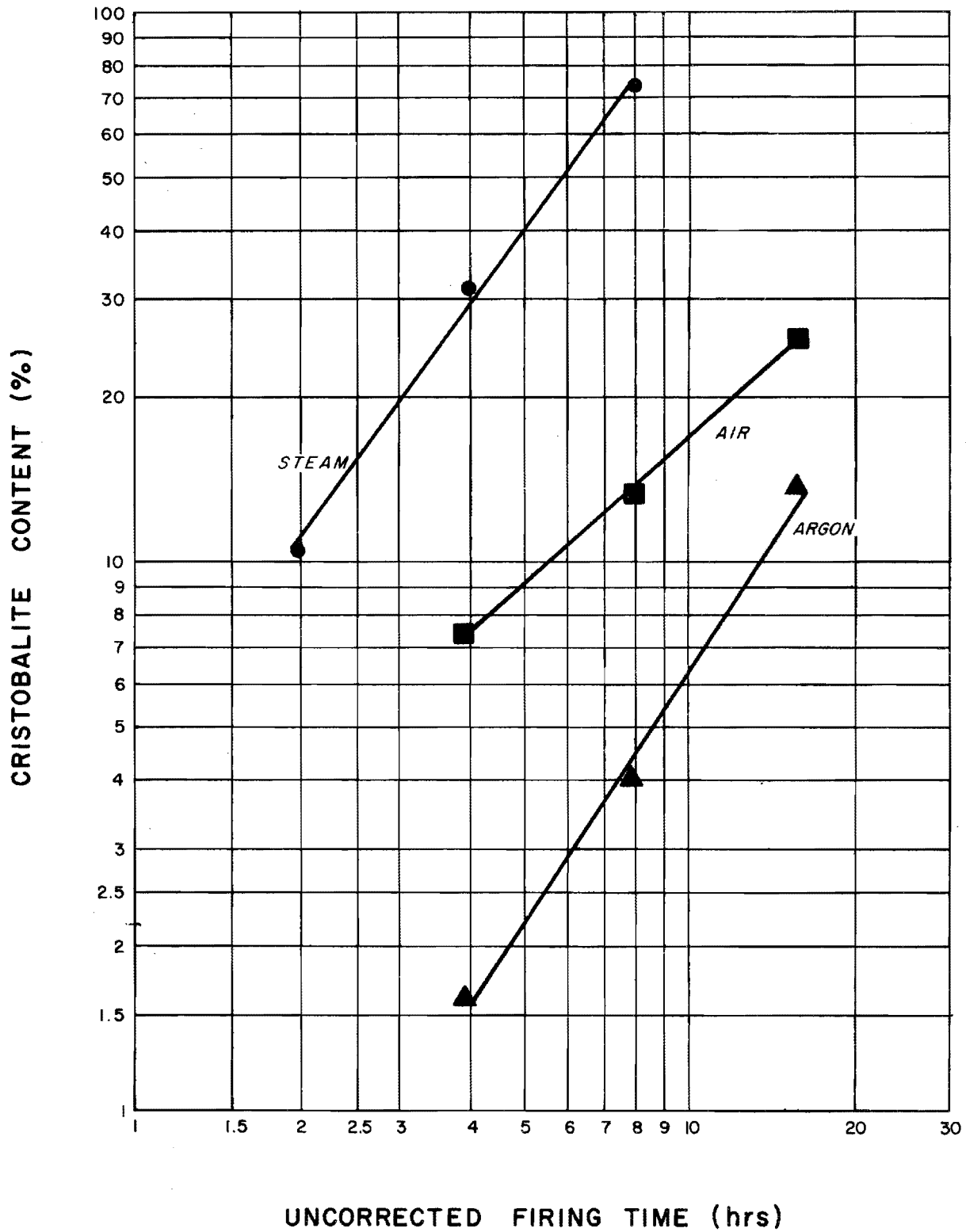


Figure 12. Cristobalite Content of Slip Cast Fused Silica as a Function of Firing Atmosphere.

increased by the steam atmosphere, indicating in turn a much greater rate of bulk diffusion. This tendency is also apparent from Figure 9 which shows that although, at two hours, the steam-fired samples had already passed the point of significant thermal fracture of the cristobalite, as seen from Figure 11, the bulk diffusion rate was high enough to produce a continuing decrease in porosity. The porosity values are quite remarkable in that they were a full 30 per cent below the lowest values reached in air firing. Firing in steam produced a decrease in porosity from the unfired value more than double that obtained with any other firing procedure. Figure 13 shows that this low porosity is not attained through the formation of closed pores since the apparent theoretical densities varied in a consistent manner with cristobalite content regardless of the firing atmosphere.

The strength data of Figure 12 indicate that much might be gained by lower temperature firing of the silica in steam. The strength attained in steam is substantially higher than that normally associated with air firing. The statistical significance of this observation could not be determined in view of the small size of the experiment.

Figure 12 shows that the steam atmosphere markedly increases the devitrification rate of the silica, an observation consistent with the literature<sup>1</sup>. Although it is difficult to quantize, this increase in devitrification rate in steam may be more than offset by the increased bulk diffusion rate.

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<sup>1</sup>Ainslie, N. G., C. R. Morelock, and D. Turnbull, "Devitrification Kinetics of Fused Silica", presented at 1961 meeting of American Ceramic Society, Philadelphia, Pennsylvania.



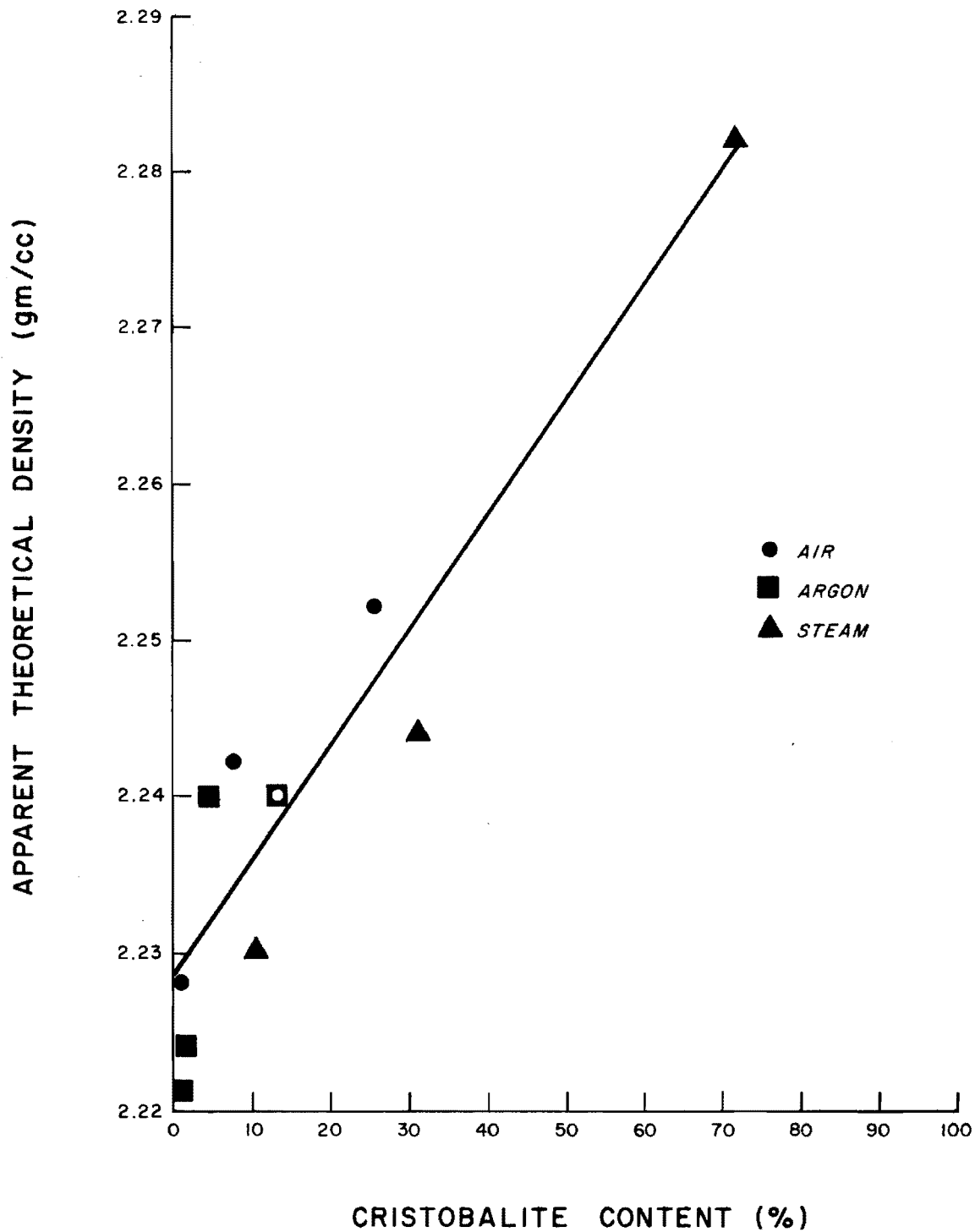


Figure 13. Apparent Theoretical Density of Slip Cast Fused Silica as a Function of Firing Atmosphere and Cristobalite Content.

The results from firing in argon were essentially the converse of those from the steam firings. It is evident that the oxygen and water molecules are quite effective in promoting atom mobility in the silica, leading to increases, over the firings in an inert atmosphere, in both bulk diffusion and devitrification. This, in turn, exerts a substantial influence on the bulk diffusion and devitrification dependent properties such as strength, porosity, cristobalite content, and bulk density.

B. Slip Cast Alumina

1. Effect of Pressure and Mold Vibration During Casting

An alumina slip was prepared by milling a mixture of 2000 gm. of 220 mesh Norton 38 Alundum, 411 ml. of de-ionized water, and 25 ml. of concentrated 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 the slip are summarized in Table XI.

TABLE XI

PROPERTIES OF ALUMINA SLIP VP-1

Solids Content	82.1 w/o
Specific Gravity	2.59
Apparent Viscosity*	2,700 cp
pH	3.9

\* Brookfield Model LVF, 30 rpm, spindle No. 3.

Three-quarter-in. diameter by 5-5/8-in. long bars were cast in one piece molds using the graphite mold release. The molds were sealed by gasketed heads, placed under pressure, and vibrated on a Syntron vibration table. Pressures of 20, 40, and 60 psig and 60 cycle axial vibration amplitudes of 0.010, 0.012, and 0.015 inches were used. Casting times were measured and the bars were dried at 230° F for 24 hours. Porosity, bulk density, and theoretical density measurements were made using air displacement and the bars were broken in three point loading. The results of the tests are summarized in Table XII.

TABLE XII  
PROPERTIES OF ALUMINA BARS  
CAST WITH PRESSURE AND VIBRATION USING SLIP VP-1

<u>Mold Pressure</u> (psig)	<u>Vibration Amplitude</u> (in)	<u>Casting Time</u> (hr)	<u>Porosity</u> (%)	<u>Bulk Density</u> (gm/cc)	<u>Theoretical Density</u> (gm/cc)	<u>Green Modulus of Rupture</u> (psi)
20	0.010	4.75	32.3	2.54	3.75	1700
20	0.012	5	31.4	2.57	3.75	1800
20	0.015	7	30.9	2.59	3.75	1800
40	0.010	1.75	32.9	2.52	3.75	1500
40	0.012	2	32.6	2.53	3.75	1600
40	0.015	4.5	31.2	2.58	3.75	1700
60	0.010	1.5	32.8	2.52	3.75	1600
60	0.012	1.75	32.7	2.52	3.74	1600
60	0.015	2	31.2	2.58	3.75	1700

The importance of vibration is shown by the significant increase in bulk density accompanying increased vibration. This undoubtedly occurred because the thixotropic slip is at least partially prevented from bridging by the vibration. Prevention of bridging would produce a more normal casting behavior and correspondingly longer casting times as well as a lower drying and firing shrinkage. Vibration also aided materially in filling the molds and producing sound castings.

The longer casting times associated with vibration were more than offset by the application of pressure. Pressure application also proved beneficial in making complex castings in unvented molds since the air was forced out through the pores in the plaster.

Although vibration and pressure caused substantial changes in the porosity and bulk density, the green strength was relatively unaffected. The benefits of pressure and vibration might be felt in more rapid strengthening during firing.

## 2. Profile Studies

Although alumina does not sinter appreciably at temperatures below 2800° F, the possibility of low temperature strengthening in slip cast alumina was obvious. This was implied by the presence of a gel, indicated by the low apparent theoretical density, which could show strengthening upon dehydration.

A slip was prepared as described in the preceding section except that only 23.5 ml of concentrated hydrochloric acid was added. The properties of the slip are summarized in Table XIII.

TABLE XIII  
PROPERTIES OF ALUMINA SLIP P-1

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

\*Brookfield Model LVF, 30 rpm, spindle No. 3.

Standard test bars were cast in one piece molds using the graphite mold release, a pressure of 60 psig, and a 60 cycle axial vibration amplitude of 0.015-in. The cast bars were air dried in the molds for 24 hours, removed from the molds, and dried at 130° F for 24 hours followed by 16 hours at 330° F. Sets of bars were heated in a tube furnace to the firing temperature at a rate of 1000° F per hour, fired for eight hours, and cooled in the furnace to avoid thermal shock. Firing temperatures were 2030° F, 2140° F, and 2250° F.

Porosity, bulk density, and theoretical density values were determined by air displacement and the moduli of rupture were measured in three point loading on a four inch span. The results of these tests are summarized in Table XIV.

Although the initial experiment was too small for statistical analysis, the data seem to support the idea of strengthening through gel dehydration. The low rate at which the strength changed with increasing firing temperature

TABLE XIV

PROPERTIES OF DRIED AND FIRED BARS CAST FROM ALUMINA SLIP P-1

<u>Firing Temperature</u> (°F)	<u>Porosity</u> (%)	<u>Bulk Density</u> (gm/cc)	<u>Linear Firing Shrinkage</u> (%)	<u>Apparent Theoretical Density</u> (gm/cc)	<u>Modulus of Rupture</u> (psi)
Unfired	32.7	2.576		3.83	
2030*	32.1	2.629	1.44	3.88	13,800
2140*	29.8	2.67	1.65	3.80	15,800
2250*	28.1	2.76	1.97	3.84	17,000

\* Fired for 8 hours

is more consistent with the dehydration mechanism than with normal sintering. The strengthening upon firing appears significant enough to warrant further firing studies. These studies will include firing at about 550-600° F where the gel dehydration should begin to appear. If substantial strengthening occurs in this firing range, the gel dehydration postulate will be confirmed since these temperatures are far too low to allow normal sintering.

The bars referred to as unfired in Table XIV are the same group as was later fired at 2030° F. An interesting observation may be made using the weights and theoretical densities before and after firing. Assuming that the unfired samples contain no closed pores and that the theoretical density is brought to 3.83 gm/cc from the theoretical density of 3.95 gm/cc for alumina by bound water contained as a gel, the density may be approximated by

$$\frac{100 + W}{\rho_o} \doteq \frac{100}{3.95} + \frac{W}{1.00}$$

where  $W = \frac{\text{gm H}_2\text{O}}{100 \text{ gm Al}_2\text{O}_3}$

$\rho_o$  = apparent theoretical density of unfired samples

Solving for the water content

$$\begin{aligned} W &\doteq \frac{100}{\rho_o - 1} \left( 1 - \frac{\rho_o}{3.95} \right) \\ &\doteq \frac{100}{3.83 - 1} \left( 1 - \frac{3.83}{3.95} \right) = 1.07 \end{aligned}$$

and the weight loss, if the water is completely removed upon firing, is approximately 1.07 per cent. The weight loss calculated from the sample weight before and after firing is also 1.07 per cent. Even the identical results of these two calculations cannot be cited as positive proof of the gel dehydration mechanism in view of the assumptions made. On the other hand, these calculations do serve as pleasing support both for the gel formation postulate and for the reliability of the air displacement system for determination of the theoretical density of porous solids. If this indication is true, the theoretical density of 3.88 gm/cc for the 2030° F firing implies that the gel dehydration does result in some closed pore formation.

C. Al-U<sub>3</sub>O<sub>8</sub> Interactions

1. Modifications in Testing Procedure

Arcing between the thermocouple post and the heating coils continued to be a problem during DTA ignition of the more energetic thermets. This was most apparent with 15 w/o Al-U<sub>3</sub>O<sub>8</sub> pellets surrounded by magnesia insulation during firing. When the pellets were fired under a pressure of 30 microns of argon, the aluminum vapor evolution was sufficient to disintegrate the pellet completely and to blow the magnesia completely out of the retaining cup. In addition, arcing caused the x-y recorder pen to undergo violent excursions. Under one atmosphere absolute of argon, the pellet remained intact although the structure was filled with voids and some arc-over remained. Under two atmospheres absolute of argon, little frothing was noted in the samples and arc-over almost disappeared completely.

In order to eliminate the effects of arc-over on the x-y recorder as much as possible, the sample holding post was modified. 3/32-in. diameter alumina spaghetti was cut to the length of the thermocouple post after one end was sealed with an arc-plasma torch. The spaghetti was placed over the thermocouple post and the sample was held on the closed end of the spaghetti. This effectively isolated the thermocouple electrically at least as far as transient arc-over was concerned. The DTA curves obtained with the closed spaghetti were quite smooth and showed little of the interaction previously common. The peak height and area were somewhat reduced by this procedure, but little change was observed in the indicated ignition temperature. Since the DTA is used for comparison purposes rather than quantitative measurements of energy release, the elimination of arc-over interference was well worth the price of decreased system sensitivity.



2. Modifications in Sample Preparation

Indications were seen in the past that blending of powders containing fine  $U_3O_8$  was inefficient since such pellets showed abnormally low ignition energy yields. A study was made to evaluate the importance of the mixing technique. Fifteen w/o Al- $U_3O_8$  pellets were compounded from Alcoa No. 140 aluminum and -325 mesh  $U_3O_8$  powders which were:

1. Blended in the usual manner without drying.
2. Blended without drying, vacuum dried for 48 hours, and blended again.
3. Blended without drying, air dried for 48 hours, and blended again.
4. Blended in methanol and air dried.

The pellets produced from the blended powders were subjected to DTA at a heating rate of 60° F per minute and under an argon pressure of 2 psig. The results of this study are shown in Table XV.

TABLE XV  
EFFECTS OF POWDER BLENDING TECHNIQUE  
ON IGNITION CHARACTERISTICS OF Al- $U_3O_8$  THERMETS

<u>Mixing Technique</u>	<u>Ignition Temperature</u> (°F)	<u>Peak Height</u> (mv)	<u>Peak Area</u> (mv-sec)
Usual	1720	5.53	202
Vacuum Dried, Reblended	1710	7.20	261
Air Dried, Reblended	1770	4.98	199
Methanol Blended, Air Dried	1680	4.30	182

The air dried powder produced higher ignition temperatures, perhaps indicative of surface oxidation of the aluminum, and no apparent improvement in blending since the peak area was little different from that with the usual blending technique. The powder blended in methanol gave a slightly lower ignition temperature, probably as a result of organic coating removal from the surface of the aluminum. Again, no indication was given of improved mixing. The vacuum dried powder gave essentially the same ignition temperature as that with the conventional powder and showed better mixing by a substantially greater peak area.

Several pellets were also blended in the normal manner but with additions of 1 w/o Baymal<sup>1</sup>. These pellets showed essentially the same increase in peak area as the vacuum mixing technique but produced much more uniform structure in the fired pellet. Studies were begun to determine the optimum Baymal content but, in the meantime, 1 w/o Baymal was used for blending pellets for the other studies and use of undried powders was continued in view of the greater experimental convenience.

### 3. Photographic Studies

Attempts were begun to follow the  $\text{Al-U}_3\text{O}_8$  reaction visually. Telephoto motion pictures were made of several pellets igniting in air. While these initial attempts involved largely uncontrolled heating rates, the results were very interesting.

Figure 14 shows a single frame and a film strip of a 14.6 w/o Al thermet igniting in an open furnace. Since the rear of the pellet was heated fastest,

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<sup>1</sup>E. I. du Pont de Nemours' colloidal hydrated alumina.

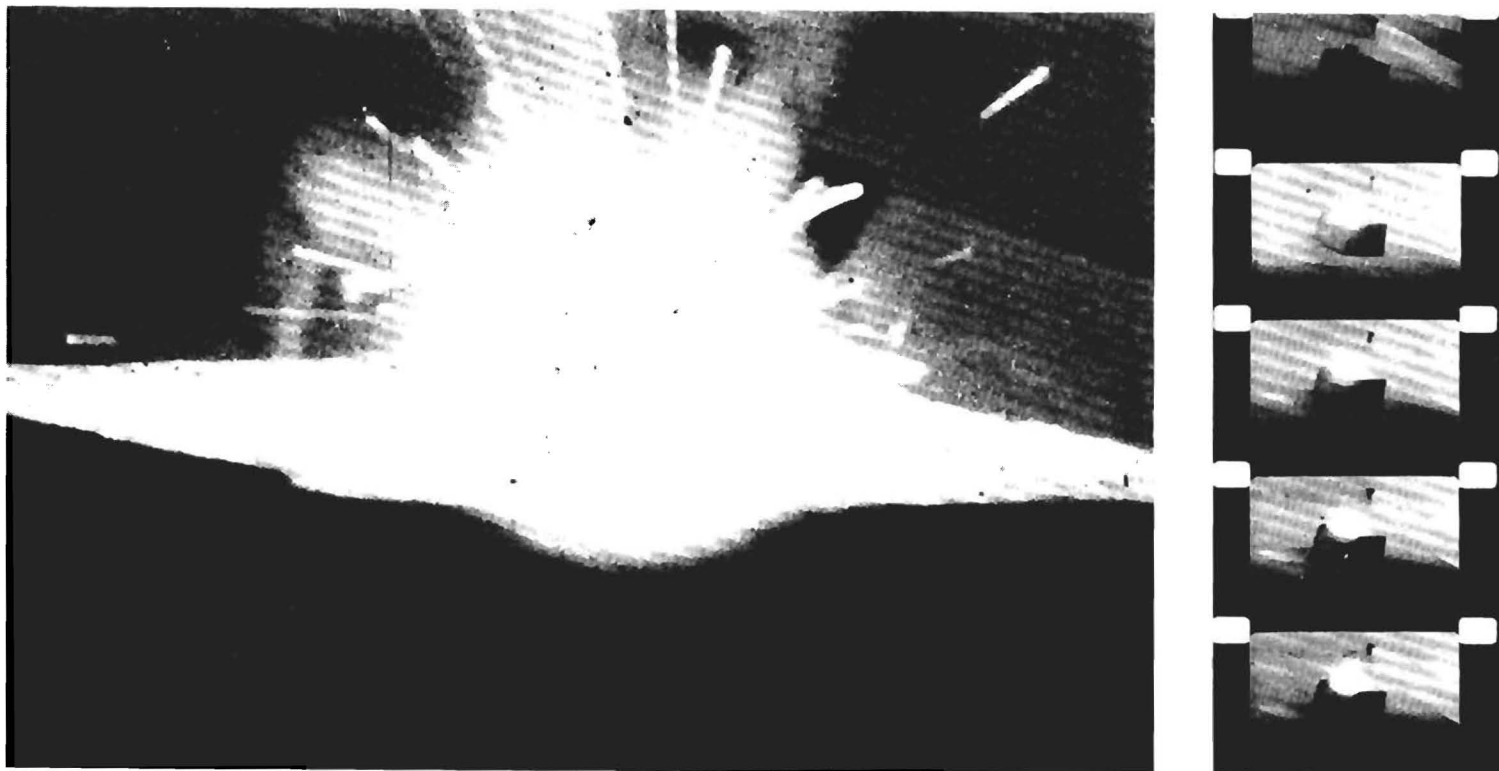


Figure 14. Frames from Motion Picture of  $\text{Al-U}_3\text{O}_8$  Thermet Igniting.

ignition began at that point in the second frame of the film strip. The ignition spread rapidly, enveloping 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 frame.

#### 4. Density of $U_3O_8$

In evaluating the results of this study with respect to other applications of Al- $U_3O_8$  dispersions, knowledge of the relationship between weight per cent and volume per cent is necessary. Since the literature value for the density of  $U_3O_8$  varies from  $7.3^1$  to  $8.39^2$ , an independent measurement appeared in order.

The density of  $U_3O_8$  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  $8.11 \pm 0.03$  gm/cc. A similar measurement was made in a Beckman Air Pycnometer. This determination gave a density of  $8.16 \pm 0.01$  gm/cc.

A cup is being machined which will permit more accurate determinations of the theoretical density to be made in the air displacement system. Upon completion, another series of density determinations will be made in which  $U_3O_8$  ground to different particle sizes will be used. This study will point out any influence, on the theoretical density, of voids within the  $U_3O_8$  particles. Until this study is completed, Figure 15 shows the best apparent correlation between weight and volume per cent in Al- $U_3O_8$  composites.

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<sup>1</sup>Etherington, "Nuclear Engineering Handbook," p. 13-77, McGraw-Hill Book Company, New York (1958).

<sup>2</sup>Wilkinson, W. D. and Murphy, W. F., "Nuclear Reactor Metallurgy", p. 149, D. Van Nostrand Co., Inc., (1958).

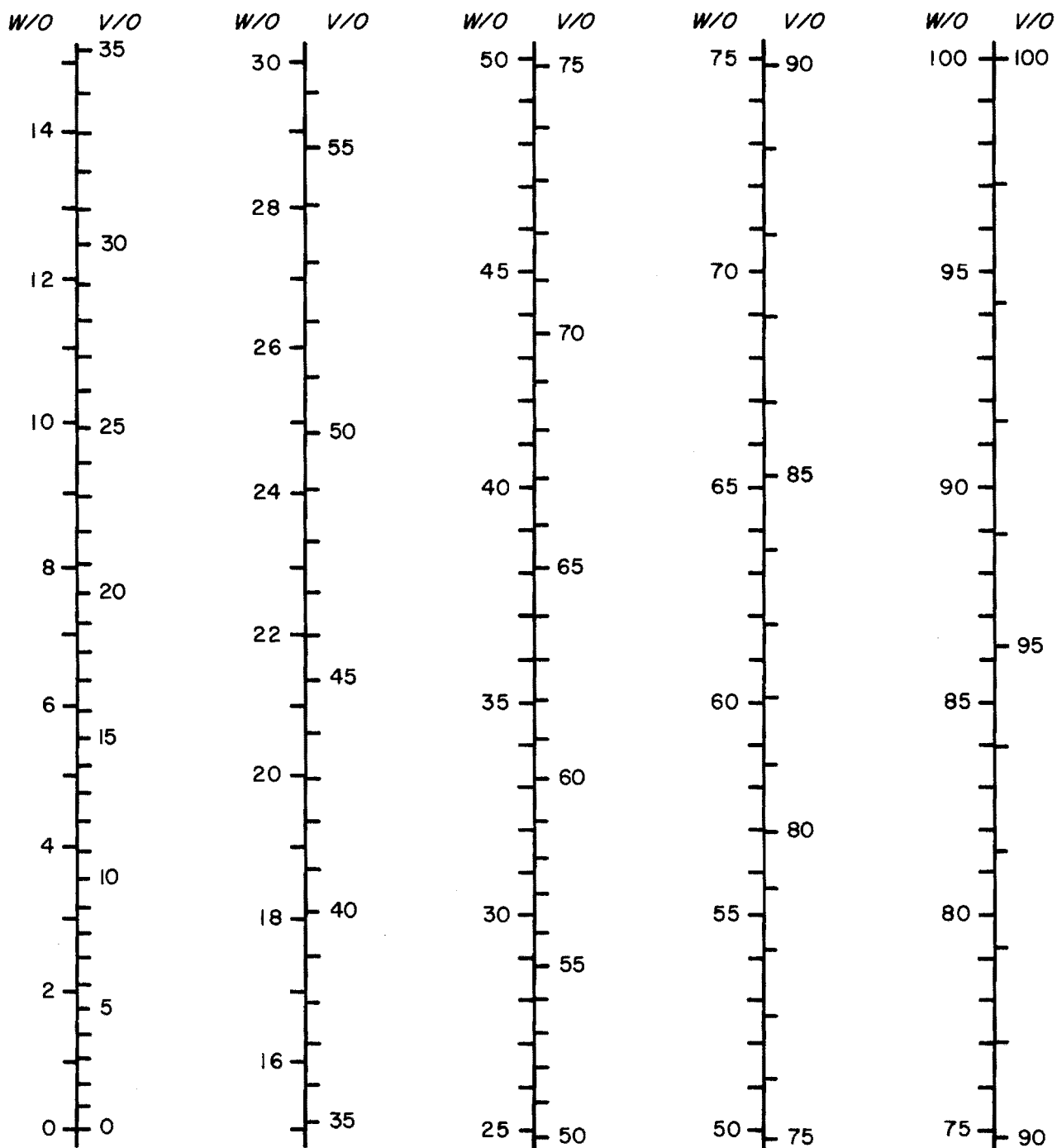


Figure 15. Conversion Scale for Weight and Volume Per Cent Al in Al - U<sub>3</sub>O<sub>8</sub> Dispersions.

5. Thermochemical Calculations

Calculations were made of the heats of formation of the uranium-aluminum intermetallic compounds to serve as a basis for estimation of the energy released from Al-U<sub>3</sub>O<sub>8</sub> reactions. The standard heats of formation of the intermetallics were taken from Ivanov<sup>1</sup>. The heat capacities were estimated by atomic contributions since no values could be found in the literature. Contributions of 6 were assumed for both U and Al. Since Al is a light element, its energies will not saturate at low temperatures and a contribution of 6 is probably high. Since the converse is true for U, however, the errors should partially compensate. The maximum error from the heat capacity approximation is estimated to be 10 per cent in the heats of formation of the intermetallics and, therefore, less than two per cent in the heats of reaction for Al-U<sub>3</sub>O<sub>8</sub> reactions. Data for the aluminum and, later, for UO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, were taken from Kubaschewski and Evans<sup>2</sup>.

The equations for the heats of formation of the intermetallics are<sup>3</sup>:

298 - 935° K

$$\begin{aligned}\Delta H_{fUAl_2} &= -23,030 + 4.73T - 6.97 \times 10^{-3}T^2 \\ &\quad - 0.233 \times 10^{-5}T^3 \text{ cal/mole}\end{aligned}\quad 5)$$

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<sup>1</sup>Ivanov, M. I., V. A. Tumbakov, and N. S. Podolskaya, "The Heats of Formation of UAl<sub>2</sub>, UAl<sub>3</sub>, and UAl<sub>4</sub>," Atomnaya Energ. 5 166-170 (1958). Each issue of this journal is completely translated into English.

<sup>2</sup>"Metallurgical Thermochemistry", Pergamon Press, New York (1958).

<sup>3</sup>The first temperature span was chosen as 298-935° K. Since Al actually melts at 933° K, this introduces a slight error because of the different heat capacity from 933-935° K. The error is extremely small, however, and one integration is eliminated.

$$\begin{aligned}\Delta H_{fUAl_3} &= -26,110 + 5.79T - 8.45 \times 10^{-3}T^2 \\ &\quad - 0.233 \times 10^{-5}T^3 \text{ cal/mole}\end{aligned}\tag{6}$$

$$\begin{aligned}\Delta H_{fUAl_4} &= -32,300 + 6.85T - 9.93 \times 10^{-3}T^2 \\ &\quad - 0.233 \times 10^{-5}T^3 \text{ cal/mole}\end{aligned}\tag{7}$$

935 - 1045° K

$$\Delta H_{fUAl_2} = -26,526 - 6.18T \text{ cal/mole}\tag{8}$$

$$\Delta H_{fUAl_3} = -31,480 - 7.18T \text{ cal/mole}\tag{9}$$

$$\Delta H_{fUAl_4} = -39,530 - 8.18T \text{ cal/mole}\tag{10}$$

1045 - 1403° K

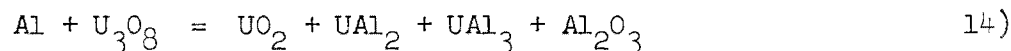
$$\Delta H_{fUAl_2} = -28,700 - 5.2T \text{ cal/mole}\tag{11}$$

$$\Delta H_{fUAl_3} = -33,650 - 6.2T \text{ cal/mole}\tag{12}$$

$$\Delta H_{fUAl_4} = -41,710 - 7.2T \text{ cal/mole}\tag{13}$$

Values calculated from Equations 5 through 13 are given in Table XVI.

The estimation of the energy release from a particular reaction is difficult in view of the variability which may occur in the products. For the Al-U<sub>3</sub>O<sub>8</sub> compacts in the range of 15 w/o, the unbalanced equation which apparently applies is



A consideration of this equation shows:

TABLE XVI

ESTIMATED HEATS OF FORMATION OF ALUMINUM-URANIUM INTERMETALLICS

$T$ (°K)	$-\Delta H_{fUAl_2}$ (kcal/mole)	$-\Delta H_{fUAl_3}$ (kcal/mole)	$-\Delta H_{fUAl_4}$ (kcal/mole)
300	22.3	25.2	31.2
400	22.4	25.3	31.3
500	22.7	25.6	31.6
600	23.2	26.2	32.3
700	23.9	27.0	33.2
800	24.9	28.1	34.4
900	26.1	29.4	35.9
935	26.6	30.0	36.5
935	32.3	38.2	47.2
1000	32.7	38.7	47.7
1045	33.0	39.0	48.1
1045	34.1	40.1	49.2
1100	34.4	40.5	49.6
1200	34.9	41.1	50.4
1300	35.5	41.7	51.1
1400	36.0	42.3	51.8



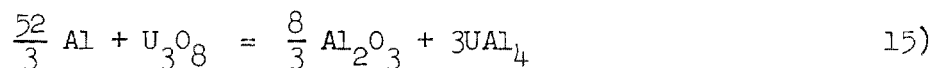
$$\text{Unknowns} = 4 \text{ (UAl}_2\text{, UAl}_3\text{, UO}_2\text{, Al}_2\text{O}_3\text{)}$$

$$\text{Balances} = 3 \text{ (Any 3 independent balances may be drawn on U, Al, O, or the overall mass.)}$$

$$F = U - B = 1$$

A degree of freedom thus exists and no explicit balance is possible. The same initial composition can lead, within limits, to several final mixtures. As an example, the limiting energy releases are shown in Figure 16 for a 14.6 w/o Al compact reacting according to Equation 14. The pertinent calculations are given in Appendix A.

The maximum credible energy release would occur from the reaction



corresponding to complete reaction of a 35.7 w/o Al compact. The calculated energy release from this reaction is shown as a function of temperature in Figure 17.

It is of interest to note that the complete reaction for any compact can be calculated knowing

1. The residual aluminum
2. The residual  $\text{U}_3\text{O}_8$ .
3. A qualitative analysis of the final mixture.
4. No further information if only one intermetallic is found in the final mixture. The amount of either  $\text{UO}_2$ ,  $\text{Al}_2\text{O}_3$ , or one of the intermetallics if the mixture contains two intermetallics. Any two amounts from the group  $\text{UO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{UAl}_2$ ,  $\text{UAl}_3$ ,  $\text{UAl}_4$  if all three intermetallics are found in the final mixture.

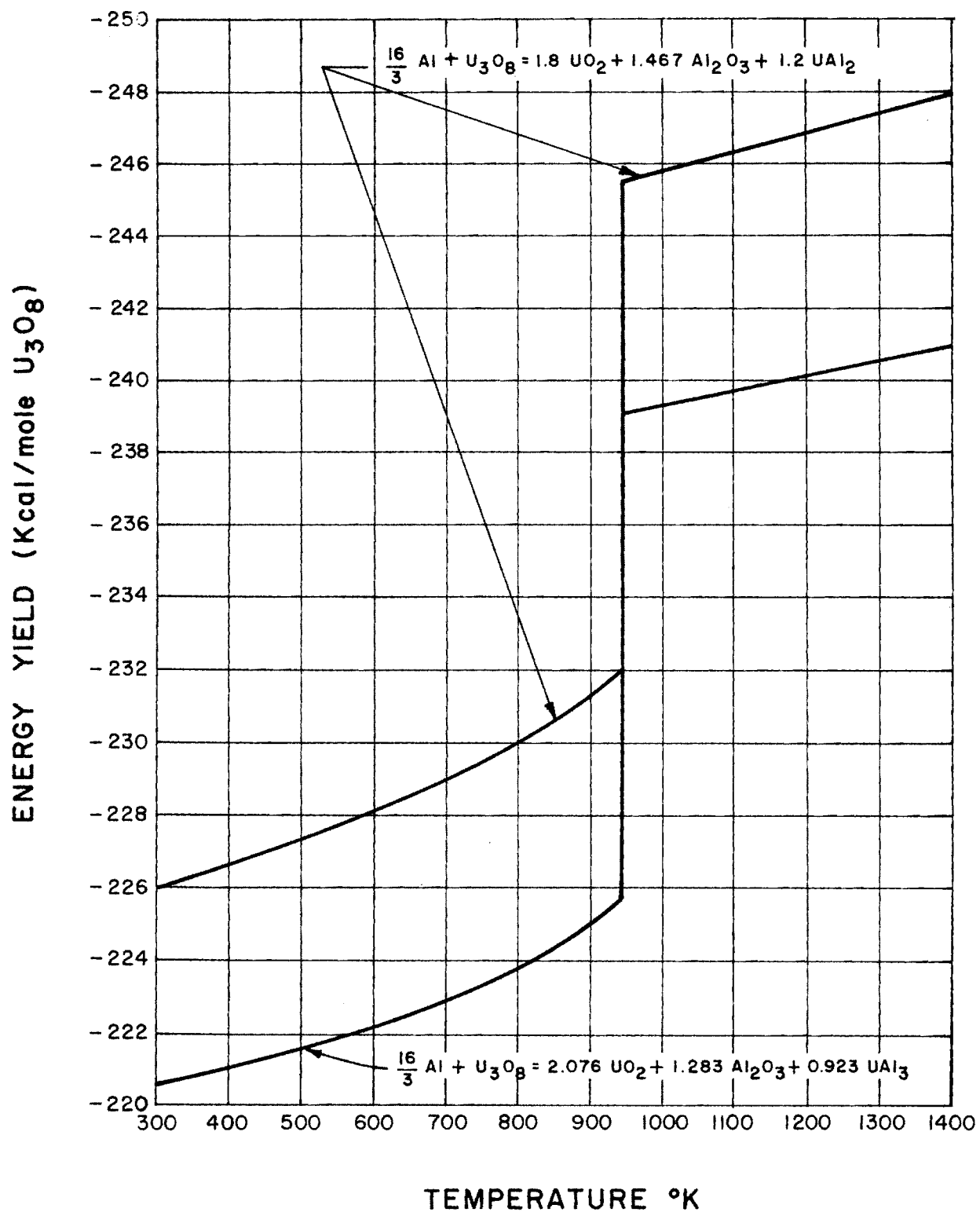


Figure 16. Limiting Energy Yields from Al- $U_3O_8$  Thermet of 14.6 w/o Al.

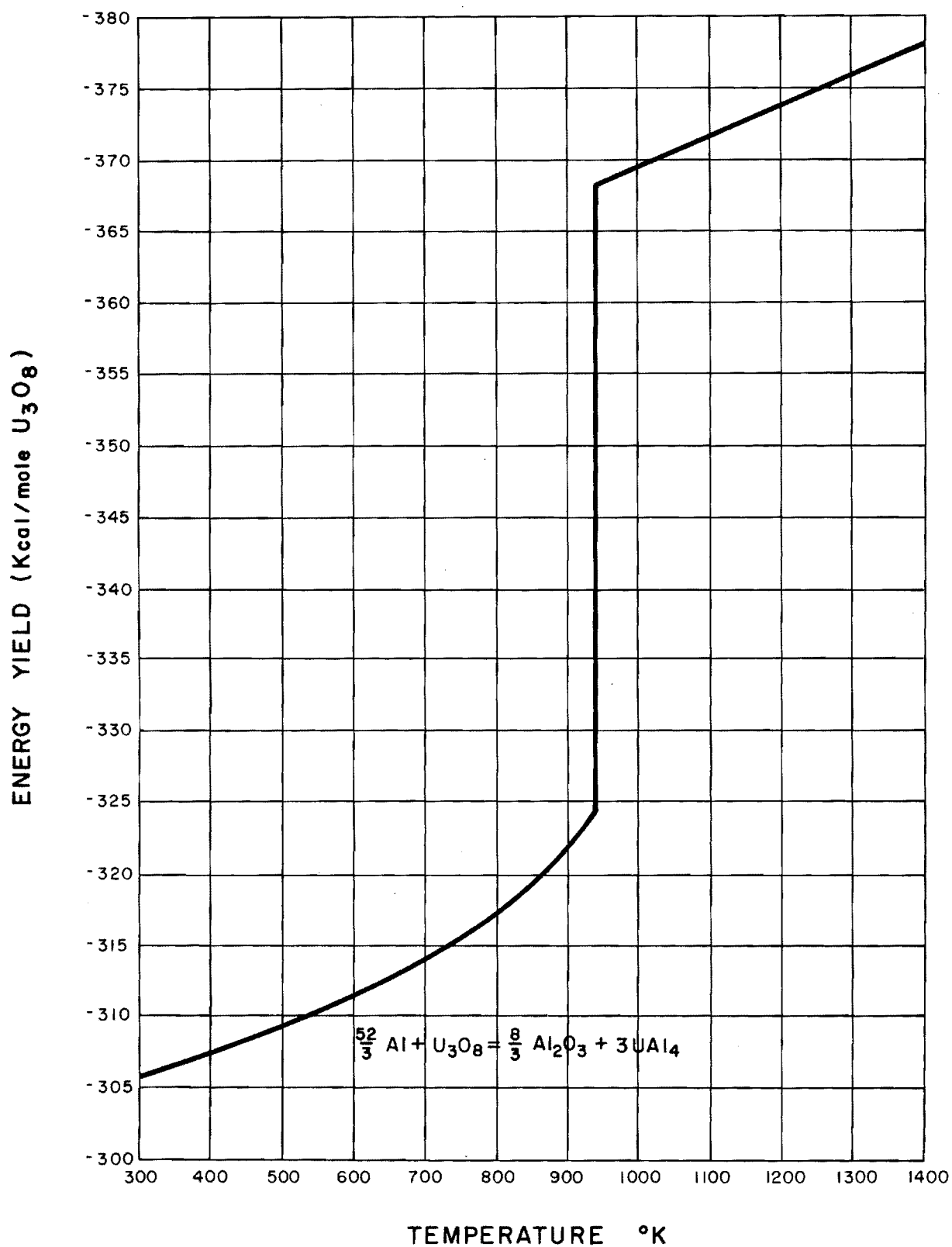


Figure 17. Maximum Energy Yield from Al- $U_3O_8$  Thermet 35.7 w/o Al.

6. Phase Identification

X-ray diffraction analysis of the thermets was begun. Numerous traces were made of reacted 14.6 w/o Al compacts. The traces were completely resolved and generally showed  $\alpha$ - $\text{Al}_2\text{O}_3$ ,  $\text{UO}_2$ ,  $\text{UAl}_2$ , and  $\text{UAl}_3$ . Only in thermets with  $\text{U}_3\text{O}_8$  particle sizes in excess of +140 mesh were traces obtained for residual  $\text{U}_3\text{O}_8$ . Although standards were not available for quantitative analysis, qualitative evaluations of the relative  $\text{UAl}_2$ : $\text{UAl}_3$  ratio showed that an increase in  $\text{UAl}_2$  corresponded to a decrease in  $\text{UAl}_3$  as predicted by Equation 16, Appendix A. In addition, the peak heights and peak areas from the DTA plot tended to be greater with increasing  $\text{UAl}_3$ , consistent with Figure 16. As the particle size of the  $\text{U}_3\text{O}_8$  increased, the relative amount of  $\text{UAl}_2$  increased, indicating less vigorous reaction. This appears consistent with the DTA analyses. Until complete quantitative analyses become available, more concrete correlations cannot be made.

A series of x-ray diffraction analyses was also completed with 59.7 w/o Al thermets which had been heated to different temperatures. The qualitative results of these analyses are summarized in Table XVII.

It is evident that the results shown by Table XVII are not completely consistent and that more tests must be made. Several conclusions seem safe, however. The 59.7 w/o Al thermet begins reacting below 1200° F with the large excess of aluminum promoting the formation of  $\text{UAl}_4$ . The absence of a  $\text{U}_3\text{O}_8$  trace in the 1200° F sample implies that the reaction may be complete even prior to the melting point of aluminum. The apparent lack of  $\text{UAl}_2$  and  $\text{UAl}_3$  in the samples heated past the peritectic decomposition temperature, 1346° F, of  $\text{UAl}_4$  and the presence of  $\text{UAl}_4$  in the 1900 and 2100° F samples

indicates that the cooling of the samples was slow enough to permit re-formation of  $UAl_4$  rather than quenching in  $UAl_2$  and  $UAl_3$ . The anomalous results of the 1300 and 2000° F samples, which show incomplete reaction of the  $U_3O_8$  demand further study.

TABLE XVII  
X-RAY DIFFRACTION ANALYSES OF 59.7 w/o  $Al-U_3O_8$  THERMETS\*

Maximum Furnace Temperature During Firing (°F)	$U_3O_8$	$UO_2$	$UAl_2$	$UAl_3$	$UAl_4$	$Al_2O_3$
1200	0	0	0	0	1	1
1300	2	1	0	T	0	0
1900	0	0	0	0	3	2
2000	1	2	T	T	0	0
2100	0	0	0	0	2	1

\* 0 designates no indication of substance

T designates trace amounts

1, 2, 3 designate relative amounts of substance, 1 = greatest, 3 = least

Chemical analyses for residual aluminum, described in Appendix B, were completed for four samples. The results are given in Table XVIII as the reacted aluminum along with calculated amounts of reacting aluminum to produce specific products.

TABLE XVIII

CHEMICAL ANALYSES FOR ALUMINUM REACTING IN Al-U<sub>3</sub>O<sub>8</sub> THERMETS

Initial Aluminum Content		Aluminum Reacting
(w/o)	(gm/100 gm initial U <sub>3</sub> O <sub>8</sub> )	(gm/100 gm initial U <sub>3</sub> O <sub>8</sub> )
14.6	17.1	16.2
14.6	17.1	16.3
35.7	55.5	20.3
59.7	148.1	47.3

Aluminum Reacting to Yield Only Product		Product
(gm/100 gm U <sub>3</sub> O <sub>8</sub> )	(w/o Al)	
4.27	4.10	UO <sub>2</sub>
36.29	26.63	UAl <sub>2</sub>
45.90	31.46	UAl <sub>3</sub>
55.50	35.69	UAl <sub>4</sub>

The results for the 14.6 w/o Al samples show that approximately 95 per cent of the aluminum reacted. Also, since the amount reacting was greater than required to reduce all the U<sub>3</sub>O<sub>8</sub> to UO<sub>2</sub>, some uranium-aluminum intermetallics must have been formed although the amounts cannot be calculated. These results confirm the x-ray analyses.

Although the 35.7 w/o thermet contained enough aluminum to form UAl<sub>4</sub> completely, less than this amount reacted. The reaction products must then

contain some lower intermetallics. Since the amount reacting was less than the necessary amount to form  $UAl_2$  completely, the reacted mixture must also contain some  $UO_2$ .

The x-ray and chemical analysis results for the 59.7 w/o thermet were not quite consistent. Since the amount of aluminum which reacted was insufficient to form  $UAl_4$  completely, the reacted mixture should have contained some  $UO_2$  or lower intermetallics. This was not confirmed by x-ray analysis of the same samples subjected to chemical analysis. These results were for only two pellets, however, and more extensive data must be obtained in order to evaluate the quantitative correlation.

Several samples of fired  $Al-U_3O_8$  thermets were sent to Advanced Metals Research, Sommerville, Massachusetts for analysis by electron microprobe. Although a complete report has not yet been received, a tentative report showed that phases were identified which contained  $UO_2$ ,  $UAl_2$ , and  $Al_2O_3$ . No  $UAl_3$  or  $UAl_4$  was found in the initial work.

#### D. Be- $U_3O_8$ Interactions

Studies were resumed with the Be- $U_3O_8$  thermets. The first composition studied contained 7.9 w/o of -325 mesh beryllium compounded in the same manner as the  $Al-U_3O_8$  thermets<sup>1</sup>. These samples showed sharp ignition peaks on DTA at 1820° F. The peak height was about double that typical of the  $Al-U_3O_8$  thermet and the peak area was almost twice as great. These preliminary results indicate that the Be- $U_3O_8$  reaction may be more energetic than the  $Al-U_3O_8$  reaction.

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<sup>1</sup>Progress Report No. 3, p. 65 (1961).

#### IV. DISCUSSION

The fair correlation of the porosity data in terms of reduced firing time, while pleasing, is probably only fortuitous. If devitrification promoted diffusion were the only mechanism operative, the success of such a correlation would not be surprising. In such a case, the similar rate of cooling through the cristobalite inversion should result in similar thermal shock conditions and thus produce minimum porosity at a constant cristobalite content. In turn, this minimum porosity should be approximately the same at any firing temperature since a given amount of devitrification should produce a given amount of diffusion, hence a fixed amount of densification. In practise, however, the minimum porosity is seen to decrease slightly with increasing firing temperature, indicating that a second mechanism of densification, probably bulk diffusion<sup>\*</sup>, is operative. The presence of bulk diffusion would tend to decrease the minimum porosity since the densification it produces would be additive. If minimum porosity does occur at a fixed cristobalite content, and a fixed densification by devitrification induced diffusion, then any active bulk diffusion would simply increase the densification which occurs by the time the critical cristobalite content forms. This in turn would lead to a lower minimum porosity. If the minimum porosity should differ appreciably with firing temperature, indicating significant bulk diffusion, the correlation would still be expected to suffice along the reduced time axis, but formation of a family of lines would be expected along the porosity axis. Within the usual firing limits, however, the bulk

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<sup>\*</sup> Bulk diffusion is used here simply to indicate a different mechanism than devitrification induced diffusion. The actual mechanics could be viscous flow, surface diffusion, etc.



diffusion appears small so that a satisfactory single line correlation was obtained. At much above 2300° F, the increased bulk diffusion would probably result in separation into several lines on the porosity axis.

The statistical analysis of the tensile test ring firings indicated that further attempts to improve the firing technique would be fruitless without redesign of the furnace. Since this would be both too expensive and too time consuming, the best course of action seems to be increasing the number of replicates at a given set of conditions and decreasing the number of points studied. Instead of determining the elevated temperature tensile strength at each 200° F increment, as originally planned, 500° F steps will be used and the sample size will be increased.

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 crushing strength 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 crushing 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 limited study carried out with firing atmosphere affects was most interesting. In view of previous work in the literature, a strong effect

on the devitrification rate was expected, but the profound effect on the fired properties was not. The results from this preliminary study indicate quite emphatically that further investigations of steam firing should be made. The importance of such a study is evident since the preliminary results imply that the service temperature limitations on slip cast fused silica may be much more strict in humid atmospheres. In addition, steam firing could have a marked effect on the economics of slip cast fused silica fabrication as well as affording better fired properties.

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  $\text{Al-U}_3\text{O}_8$  investigation, particularly with respect to application of these results to hazards evaluation of  $\text{Al-U}_3\text{O}_8$  dispersion fuels. At all times, the nature of the reacted  $\text{Al-U}_3\text{O}_8$  system must be kept in mind. Since the reacted mixture contains  $\text{UAl}_2$ ,  $\text{UAl}_3$ , and  $\text{UAl}_4$ , the determination of the energy release spectrum is not independent of the thermal kinetics of the environment. Upon ignition, for instance, solid  $\text{UAl}_2$ ,  $\text{UAl}_3$ ,  $\text{UO}_2$ , and  $\text{Al}_2\text{O}_3$  should first form since the ignition temperature is below the melting points of these products. A considerable amount of the energy evolved by the  $\text{Al-U}_3\text{O}_8$

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  $\text{Al-U}_3\text{O}_8$  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  $\text{UAl}_4$ . In a 35.7 w/o Al dispersion, the composition required for complete formation of  $\text{UAl}_4$ , this alone would reduce the maximum energy yield from about 1.84 Mw-sec/Kg  $\text{U}_3\text{O}_8$  to about 1.7 Mw-sec/Kg  $\text{U}_3\text{O}_8$ , a substantial change.

Evidently, then, data which will allow interpretation of the  $\text{Al-U}_3\text{O}_8$  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  $\text{Al-U}_3\text{O}_8$  mixtures may be obtained in the future report periods.

The combined chemical and qualitative x-ray analysis results provide a fair picture of the reaction results in the thermet compositions studied so far. Since quantitative chemical analysis for all reaction products would be too time consuming, however, a need for quantitative x-ray standards is apparent. Such standards will be developed during the next contract year.

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:

Mr. Paul Boland	Group Leader
Mr. S. H. Bomar	Group Leader
Mr. A. R. Colcord	Group Leader
Dr. R. F. Hochman	Research Associate
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
Mr. W. M. Linstrom	Technician
Mr. P. S. Matrangos	Technician
Mr. G. L. Maynard	Technician
Mr. G. W. Smith	Technician

Submitted by:

J. D. Fleming  
Senior Investigator

Approved:

J. W. Johnson  
Assistant Project Director

J. D. Walton, Head  
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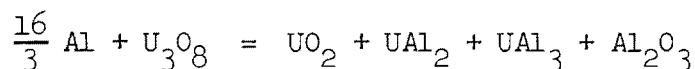
F. Bellinger, Chief  
Material Sciences Division

VI. APPENDICES

APPENDIX A

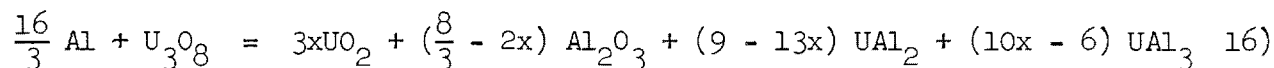
CALCULATION OF ENERGY RELEASE FROM THERMET REACTION

For a dispersion of 14.6 w/o aluminum and 85.4 w/o  $U_3O_8$ , X-ray and chemical analyses indicate the unbalanced reaction to be



Since a degree of freedom exists, this equation cannot be balanced explicitly.

A relative balance may be drawn by exercising the degree of freedom to fix any one of the four products. Fixing the  $UO_2$  in terms of the  $U_3O_8$  which reacts to form  $UO_2$  gives



by a material balance where

$$x = \frac{U_3O_8 \rightarrow UO_2}{\text{mole } U_3O_8 \text{ originally present}}.$$

For any particular temperature, x will have a certain value for which the energy release will be maximized. The energy balance for this reaction is

$$\begin{aligned} \Delta H_R = & 3x(\Delta H_{fUO_2}) + \left(\frac{8}{3} - 2x\right) \Delta H_{fAl_2O_3} + (9 - 13x) \Delta H_{fUAl_2} \\ & + (10x - 6) \Delta H_{fUAl_3} - \Delta H_{fU_3O_8}. \end{aligned} \quad 17)$$

$$\text{Let } a = \Delta H_{f\text{UO}_2}$$

$$b = \Delta H_{f\text{Al}_2\text{O}_3}$$

$$c = \Delta H_{f\text{UAl}_2}$$

$$d = \Delta H_{f\text{UAl}_3}$$

$$e = \Delta H_{f\text{U}_3\text{O}_8}$$

Then

$$\Delta H_R = 3ax + \left(\frac{8}{3} - 2x\right)b + (9 - 13x)c + (10x - 6)d - e$$

$$\frac{d(\Delta H_R)}{dx} = 3a - 2b - 13c + 10d$$

There is thus no point of mathematical maximum or minimum. Whether the slope is positive or negative depends solely on the relative magnitudes of the heats of formation. At a given temperature, the sign of the slope does not change within the limits of  $x$ .

For the 14.6 w/o Al mixture, the limits on  $x$  are set by the coefficient of  $\text{UAl}_2$  and  $\text{UAl}_3$ . Since neither is less than zero,

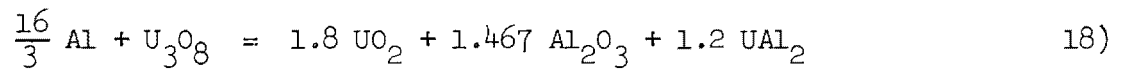
$$10x_{\min} - 6 = 0$$

$$x_{\min} = 0.6$$

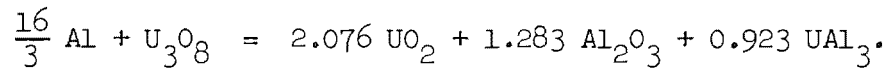
$$9 - 13x_{\max} = 0$$

$$x_{\max} = 0.6923.$$

For these two limiting conditions, Equation 16 becomes



and



The corresponding energy balances are

$$(\Delta H_R)_{\max} = 1.8 \Delta H_{f\text{UO}_2} + 1.467 \Delta H_{f\text{Al}_2\text{O}_3} + 1.2 \Delta H_{f\text{UAl}_2} - \Delta H_{f\text{U}_3\text{O}_8} \quad 19)$$

and

$$(\Delta H_R)_{\min} = 2.076 \Delta H_{f\text{UO}_2} + 1.283 \Delta H_{f\text{Al}_2\text{O}_3} + 0.923 \Delta H_{f\text{UAl}_3} - \Delta H_{f\text{U}_3\text{O}_8} \quad 20)$$

These two equations were evaluated using the data from Table XVI and values for the heats of formation of  $\text{UO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{U}_3\text{O}_8$  from Kubaschewski and Evans. The results are plotted as Figure 16.



APPENDIX B

CHEMICAL ANALYSIS OF THERMETS

A. Residual Aluminum Determination

1. Break up pellet with mortar and pestle and record original weight.
2. Place powder in an appropriate amount of 1 N NaOH. Heat on electric hot plate for one to two hours. The amount of NaOH used will depend upon the amount of residual aluminum in the pellet. For a 5 gram pellet of 15 w/o aluminum about 150 ml of solution should be used. For a 5 gram pellet of 60 w/o aluminum about 400 ml should be used. These amounts of 1 N NaOH are sufficient for complete dissolution of all the aluminum in the pellet before firing.
3. Filter through fine filter paper and wash several times with 25 ml portions of water. Retain solids and paper for determination of intermetallics and residue.
4. Make filtrate acidic by addition of 1 N HCl.
5. Dilute solution to 500 ml and pipette portion for analysis into 100 ml beaker. The quantity needed for analysis depends on the amount of aluminum present. It should contain about 10 mg of aluminum. As a guide about 50 ml should be used for residual aluminum determination on a 15 w/o thermet. A 5 ml aliquot is a good starting point for anything up to a 60 w/o thermet pellet. Add enough water to make the solution in the beaker about 50 ml.
6. Add concentrated  $\text{NH}_4\text{OH}$  dropwise until a precipitate just begins to form. Add one or two drops of acetic acid to dissolve precipitate.
7. Heat the solution to approximately  $80^\circ \text{C}$  ( $176^\circ \text{F}$ ).
8. Add slowly 4.0 to 4.5 ml of the oxine solution. Stop when solution becomes distinctly yellow.

9. If a precipitate has not already formed, add slowly 2 N  $\text{CH}_3\text{COONH}_4$  solution until a precipitate forms.
10. Add 13 to 15 ml of the  $\text{CH}_3\text{COONH}_4$  solution.
11. Let the solution stand at room temperature without stirring for at least one hour.
12. Weigh a clean sintered glass Pyrex filter crucible which has been dried in a  $130^\circ \text{C}$  oven for several hours.
13. Filter solution through tared crucible with suction. Wash all precipitate from beaker into crucible with cold water. Wash precipitate thoroughly with cold water.
14. Dry precipitate and crucible for one to two hours in  $130^\circ \text{C}$  ( $266^\circ \text{F}$ ) oven, then cool for 10 minutes and weight.
15. Calculations:

$$A = \text{dilution factor} = \frac{500 \text{ ml}}{\text{vol aliquot}}$$

$$B = \text{weight of } \text{Al}(\text{C}_9\text{H}_6\text{ON})_3 \text{ precipitate, gms}$$

$$\text{Weight of Al in sample, gms} = (0.05874)(A B)$$

B. Determination of Aluminum in Uranium-Aluminum Intermetallics

1. Wash thoroughly all solids from the filter paper in step 3 of the previous section into a 500 ml beaker, using about 250 ml of 1 N  $\text{H}_2\text{SO}_4$  for the wash liquid. Scrape part of the softened paper into the solution if necessary. This quantity of acid is sufficient for any 5 gm thermet pellet. Heat on electric hot plate for one to two hours.
2. Filter through fine filter paper and wash with water. Retain solids and paper for determination of uranium oxides and  $\text{Al}_2\text{O}_3$ .

3. Add  $\text{NH}_4\text{OH}$  until solution is only slightly acid with  $\text{H}_2\text{SO}_4$ . Dilute to 500 ml and pipette a 25 ml aliquot into a beaker. The size of this aliquot may be varied depending on the amount of aluminum present in the intermetallic cut. Keep remainder of solution for uranium determination.

4. Dilute the aliquot to a volume of about 100 ml.

5. Add slowly about 15 ml of the oxine solution.

6. Cautionusly neutralize with a saturated solution of  $\text{NH}_4\text{CO}_3$ . Add an excess of 25 ml per 100 ml of solution. (add about 30 ml excess)

7. Heat solution on electric hot plate to about  $50^\circ \text{C}$  ( $122^\circ \text{F}$ ), taking care to avoid excessive effervescence caused by too rapid heating. Digest until precipitate becomes dense and crystalline.

8. Cool, filter, and weigh as in steps 12 through 15 of the previous section. (section A)

#### C. Determination of Uranium in Uranium-Aluminum Intermetallics

1. General Remarks: The following cations interfere with the titration in this determination:  $\text{Cu(II)}$ ,  $\text{Fe(II and III)}$ ,  $\text{Mo(VI)}$ ,  $\text{Ni(II)}$ , and  $\text{Ti(IV)}$ . Since neither Al or Be cations interfere, they need not be separated from the solution to be titrated. The test portion is cooled in an ice bath after the reduction and addition of the reagents because the end point is more readily detected if the solution is cold. The addition of  $\text{FeCl}_3$  and of  $\text{H}_2\text{SO}_4$  in  $\text{H}_3\text{PO}_4$  mixtures also aids in producing a sharper end point. It has been found experimentally that when reagents of the specifications given herein are used, the blank on the reagents is negligible.

2. If the Jones reductor is new or has been standing for some time, pour 100 ml of 5 per cent  $\text{H}_2\text{SO}_4$  through the reductor; otherwise omit this step. The amalgam should be covered with water during periods when the reductor is not in use.

3. Pipette 15 ml of the stock solution from step 3 of the previous section (section B) into the Jones reductor.

4. Open the stopcock on the Jones reductor and collect the solution in a 500 ml filter flask at a rate of 8 to 10 ml per minute.

5. While the sample solution is still above the amalgam, wash the sample from the amalgam with approximately 100 ml of 5 per cent  $\text{H}_2\text{SO}_4$ . Keep the surface of the liquid above the amalgam at all times.

6. Close the stopcock and remove the filter flask.

7. Place a gas dispersion tube into the solution and bubble air through the solution for 15 minutes. Regulate the air flow so that the solution does not spatter onto the sides of the flask. This oxidizes any trivalent uranium to the quadrivalent state.

8. Add 40 ml of the  $\text{FeCl}_3$  solution.

9. Add 15 ml of the  $\text{H}_2\text{SO}_4$ - $\text{H}_3\text{PO}_4$  mixture.

10. Place the flask in an ice bath to cool for 30 minutes.

11. Add 10 drops of cold diphenylaminesulfonic acid indicator solution.

12. Titrate the solution with standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, stirring it vigorously, until the indicator changes from a light brown to a purple color, which persists for at least 30 seconds.

13. Record the volume (T) of the standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution required.

14. Calculations:

$$A = \text{dilution factor} = \frac{500 \text{ ml}}{\text{vol aliquot}}$$

$$T = \text{volume of } K_2Cr_2O_7 \text{ solution used, ml}$$

$$N = \text{normality of standard } K_2Cr_2O_7 \text{ solution} = 0.0500$$

$$119 = \text{equivalent weight of uranium}$$

$$\text{Weight of U in sample, gms} = (0.119)(T N A)$$

D. Determination of Uranium in Uranium Oxides

1. Wash all solids from the filter paper in step 2 of section B into a 250 ml beaker with about 100 ml of 1 N  $HNO_3$ . Heat on electric hot plate for one to two hours.

2. Filter through a small diameter, low ash filter paper and wash with water. Retain paper for  $Al_2O_3$  determination.

3. Add 10 ml of concentrated  $H_2SO_4$  to the filtrate and boil until strong fumes of  $SO_3$  appear.

4. Dilute filtrate to 500 ml. Proceed through steps 2 through 14 of section C. A 20 or 30 ml sample aliquot may be required for this determination.

E. Determination of Aluminum Oxide

1. Place the precipitate and filter paper from step 2 of section D in a tared porcelain crucible with cover.

2. Ignite in a furnace at  $2200^\circ F$  for about 30 minutes. Cool in air to about  $400-600^\circ F$  then cool to room temperature in a desiccator.

3. Remove crucible from desiccator and let stand in air for 10 minutes. Weigh crucible.

4. Calculations:

$$\text{Wt Al, gms} = (0.5291) (\text{wt Al}_2\text{O}_3, \text{gms})$$

F. Apparatus and Reagents

1. Jones Reductor, 5/8-in. ID and 18-in. length, equipped with an oblique-bore stopcock. Fill the tube with water, add four 1/2-in. lengths of 5-mm glass tubing and a small wad of glass wool to support the zinc amalgam. Then fill the tube to within 4 in. of the top with granulated zinc amalgam (reagent 14). Add the amalgam in small portions (sufficient to fill 1 to 2 in. of the tube), tamping each portion gently into place with a glass rod. The tamping is done to prevent the formation of air pockets or channels.

2. Use distilled water for the preparation of all reagents and throughout the procedure. All reagents should be reagent grade.

3. Ammonium Acetate Solution, approximately 2 N  $\text{CH}_3\text{COONH}_4$ . Dissolve 154 g of  $\text{CH}_3\text{COONH}_4$ , A.C.S. reagent grade, in distilled water and dilute the solution to 1 liter with distilled water.

4. Oxine Solution, 5.0 % in approximately 2 N acetic acid. Dissolve  $5.00 \pm 0.05$  g of oxine (8-hydroxyquinoline), A.C.S. reagent grade, and 11.46 ml of conc. acetic acid in distilled water and dilute to 100 ml with distilled water.

5. Diphenylaminesulfonic Acid Indicator Solution, approximately 0.01 M diphenylaminesulfonate. Mix 0.32 g of barium diphenylaminesulfonate with 100 ml of water, and then add 3 ml of conc.  $\text{H}_2\text{SO}_4$ . Heat the solution to boiling and digest it for 10 minutes. Let the barium sulfate settle out, and then decant the supernatant liquid; filter the liquid if necessary. Store the solution in a refrigerator.

6. Ferric Chloride Solution, approximately 8%  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . Dissolve 80 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in water and dilute the solution to one liter with water.

7. Mercuric Chloride Solution, approximately 6%  $\text{HgCl}_2$ . Dissolve 6 g of  $\text{HgCl}_2$  in 100 ml of water, and then add 1 to 2 drops of conc.  $\text{H}_2\text{SO}_4$ .

8. Nitric Acid, approximately 0.5%  $\text{HNO}_3$ . Dilute 1 ml of conc.  $\text{HNO}_3$  to 200 ml with water.

9. Standard Potassium Dichromate Solution, 0.0500 N  $\text{K}_2\text{Cr}_2\text{O}_7$ . Dry a quantity of a National Bureau of Standards standard sample of  $\text{K}_2\text{Cr}_2\text{O}_7$  at  $110^\circ \text{C}$  and cool it in a desiccator. Dissolve  $4.904 \pm 0.001$  g of the dry  $\text{K}_2\text{Cr}_2\text{O}_7$  in water and dilute the solution to 2 liters.

10. Sulfuric acid, approximately 9.5 v/o  $\text{H}_2\text{SO}_4$ . Carefully add 1 ml of conc.  $\text{H}_2\text{SO}_4$  to a volume of water, and then dilute the solution to 200 ml with water.

11. Sulfuric Acid, approximately 5%  $\text{H}_2\text{SO}_4$ . Carefully add 50 ml of conc.  $\text{H}_2\text{SO}_4$  to about 500 ml of water and dilute the solution to one liter with water.

12. Sulfuric Acid-Phosphoric Acid Mixture, 1:3. Mix 2 liters of conc.  $\text{H}_2\text{SO}_4$  with 6 liters of 85%  $\text{H}_3\text{PO}_4$ .

13. Zinc Metal. analytical reagent grade, 20 mesh, for use in Jones reductor.

14. Zinc Amalgam, 2%. Clean 180 g of 20-mesh size, granulated zinc by washing it with 100 ml of 0.5%  $\text{HNO}_3$ . Rinse the zinc three times with 100-ml portions of water, activate the zinc by washing it with 5%  $\text{H}_2\text{SO}_4$  for 10 seconds. Rinse the zinc rapidly with three 100-ml portions of water; then amalgamate it immediately by stirring it with 100 ml of a

HgCl<sub>2</sub> solution for 10 minutes. Remove the solution by decantation and rinse the amalgam 3 to 4 times with 100-ml portions of 0.5% H<sub>2</sub>SO<sub>4</sub>. Store the amalgam under water.

G. References

TID 7015, ORNL Master Analytical Manual, Procedures Numbered 1 210250 (5-18-53) and 1 219270 (6-1-56)

Lundell, G. E. F., and H. B. Knowles; "Use of 8-Hydroxyquinoline in Separations of Aluminum," Bur. Standards J. Research, 3, 91, (1929)

Kolthoff, I. M., and E. B. Sandell; Textbook of Quantitative Inorganic Analysis, 3rd Ed., The Macmillan Company, New York, 1952.



VII. PRIOR REPORTS

Previous reports issued under this contract are:

1. Monthly Letter Reports Nos. 1 - 40. Issued each month since December 1958.
2. Progress Report No. 1, August 1959. Issued as ORO-209 by OTS, Department of Commerce.
3. Progress Report No. 2, Part 1, August 1960. Issued as ORO-325 by OTS, Department of Commerce.
4. Progress Report No. 2, Part 2 (Declassified), August 1960.
5. Progress Report No. 3, August 1961.

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QUARTERLY REPORT NO. 2

PROJECT NO. B-153

MATERIALS FOR HIGH TEMPERATURE  
NUCLEAR ENGINEERING APPLICATIONS

By J. D. Fleming, J. W. Johnson, Paul Boland,  
S. H. Bomar, and A. R. Colcord

Prepared for  
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Oak Ridge, Tennessee

1962



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Engineering Experiment Station

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Atlanta, Georgia

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

QUARTERLY REPORT NO. 2

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Oak Ridge Operations Office  
Oak Ridge, Tennessee

JULY 1 to OCTOBER 1, 1962

Quarterly Report No. 2, Project No. B-153

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Quarterly Report No. 2, Project No. B-153

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 to October 1, 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 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 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 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  $U_3O_8$ . Since Al- $U_3O_8$  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

More detailed studies were made of the effects of steam on the firing behavior of slip cast fused silica. Firings were made in a tube furnace at a steam flow rate of approximately 17 cu. ft. per hour, STP, to determine the rough temperature for peak strengthening in 4 hours. A firing profile was then determined for this temperature, 2075° F, showing a peak strength of 6000 psi at 6 hours, approximately 25 per cent higher than the peak strength in air firing. The results of this firing profile study were highly erratic and indicated that the tube furnace was not suitable for steam firing. Construction of an Inconel steam firing chamber was begun to provide more uniform firing conditions.

Determination of the compressive strength of slip cast fused silica was completed. The maximum compressive strength was reached in approximately the same firing time, at a given temperature, as the minimum porosity and at a somewhat longer firing time than for maximum modulus of rupture. The maximum compressive strength ranged from 21,000 psi at a firing temperature of 2100° F to 29,500 psi at 2300° F.

The bulk density changes in slip cast fused silica were found to follow the relationship

$$\Delta B = \left[ \exp \left( 20.2 - \frac{62200}{T} \right) \right] \ln (\theta_c + 1)$$

where  $\Delta B$  is the change in bulk density.  $T$  is the firing temperature, and  $\theta_c$  is the corrected firing time. This equation was applied to a functional analysis of non-Newtonian viscous flow as a sintering mechanism for slip cast fused silica. This analysis indicated that the activation energy for sintering of slip cast fused silica is 68.6 kcal per mole.

A statistical study was made of the effects of 0.1 and 1 w/o additions of Baymal on the ignition characteristics of 14.6 w/o Al-U<sub>3</sub>O<sub>8</sub> 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. X-ray diffraction analysis did not show any obvious differences in the pellets.

The effects of U<sub>3</sub>O<sub>8</sub> particle size were studied in 25 w/o-Al-U<sub>3</sub>O<sub>8</sub> composites. Only the -325 mesh U<sub>3</sub>O<sub>8</sub> showed significantly different ignition characteristics, yielding decreased ignition temperatures and increased differential thermal analysis peak areas. Weight changes were monitored in the 25 w/o pellets but no systematic differences were noted. The weight change averaged a loss of approximately 5 w/o. Only in one pellet was an apparent weight increase noted during ignition.

One differential thermal analysis furnace was converted to chromel-alumel thermocouples to give increases sensitivity. Fifty w/o Al-U<sub>3</sub>O<sub>8</sub> composites were pressed using "dead-burned" Y-12 U<sub>3</sub>O<sub>8</sub> supplied by ORNL. Differential thermal analysis was applied to these pellets using various standards. No standard was sufficiently matched to the unknown to permit any conclusions to be drawn concerning low temperature reactions. Apparent reactions were seen in the range of 1700-1840° F regardless of the standard used.

### III. EXPERIMENTAL WORK

#### A. Slip Cast Fused Silica

##### 1. Steam Firing

Work carried out in the previous report period showed that firing slip cast fused silica in steam produced properties markedly different from those of air-fired silica. These studies showed a substantial increase in the strengthening kinetics as well as a noticeable increase in peak strength. This phenomenon is of importance in predicting firing behavior in gas fired kilns as well as representing a potential source of higher mechanical properties.

Further studies were made during this report period to confirm the previous rough results and to provide a more quantitative evaluation of the differences between steam and air firing. In these tests, slip cast fused silica bars were fired in sets of 12 in a tube furnace through which steam was passed at a rate of approximately 17 cu. ft. per hour, STP. No attempt was made to correct the firing time in these initial runs.

Since the first steam firings at 2200° F showed the bars to be overfired at 2 hours, runs were first made to determine a suitable firing temperature for production of peak strength in the range of 4 hours. This temperature proved to be about 2075° F. Following location of the convenient firing temperature range, determination of a firing profile was begun. Duplicate sets of bars were fired at each time to permit statistical analysis of the data. Following the firing, the bars were tested for porosity, bulk density, apparent theoretical density, and strength.

Upon compilation of the data, it was immediately obvious that statistical analysis was not warranted. The results showed both radical random scatter

and systematic differences. The ends of the bars closest to the steam inlet were consistently lower in strength than the ends away from the steam inlet, indicating rather pronounced axial temperature gradients in the tube. Bars in certain positions in the tube were substantially weaker than the average in almost every case, indicating nonuniform steam flow and radial temperature gradients. The bulk density measurements showed conclusively that the test runs suffered from poor control since the bulk density did not consistently increase with time. This behavior was not observed in any firings prior to this study and undoubtedly reflects both temperature and steam flow variations.

Although the tube furnace proved totally unsuitable for controlled steam firing, the results are interesting for purposes of comparison with air firing. The midline strength of the bars is shown in Figure 1 as a function of time for steam firing at 2075° F and for air firing, in the tube furnace, at 2200° F. The bars fired in steam were strengthened essentially as rapidly as the bars fired in air at a temperature 125° F higher. The contrast between steam and air firing is graphically illustrated by comparing the time of 49 hours to reach maximum strength in air firing at 2100° F with the 6 hours required in steam firing at 2075° F.

The peak strength reached in steam firing was 20-25 per cent higher than the peak strength associated with air firing. The average strength in one set of bars was 7080 psi and many individual bars had strengths in the range of 7000-9000 psi.

The results of this study showed great promise for steam firing and a demand for better firing control in order to obtain more meaningful data. The tube furnace used is unsatisfactory for this application. Construction

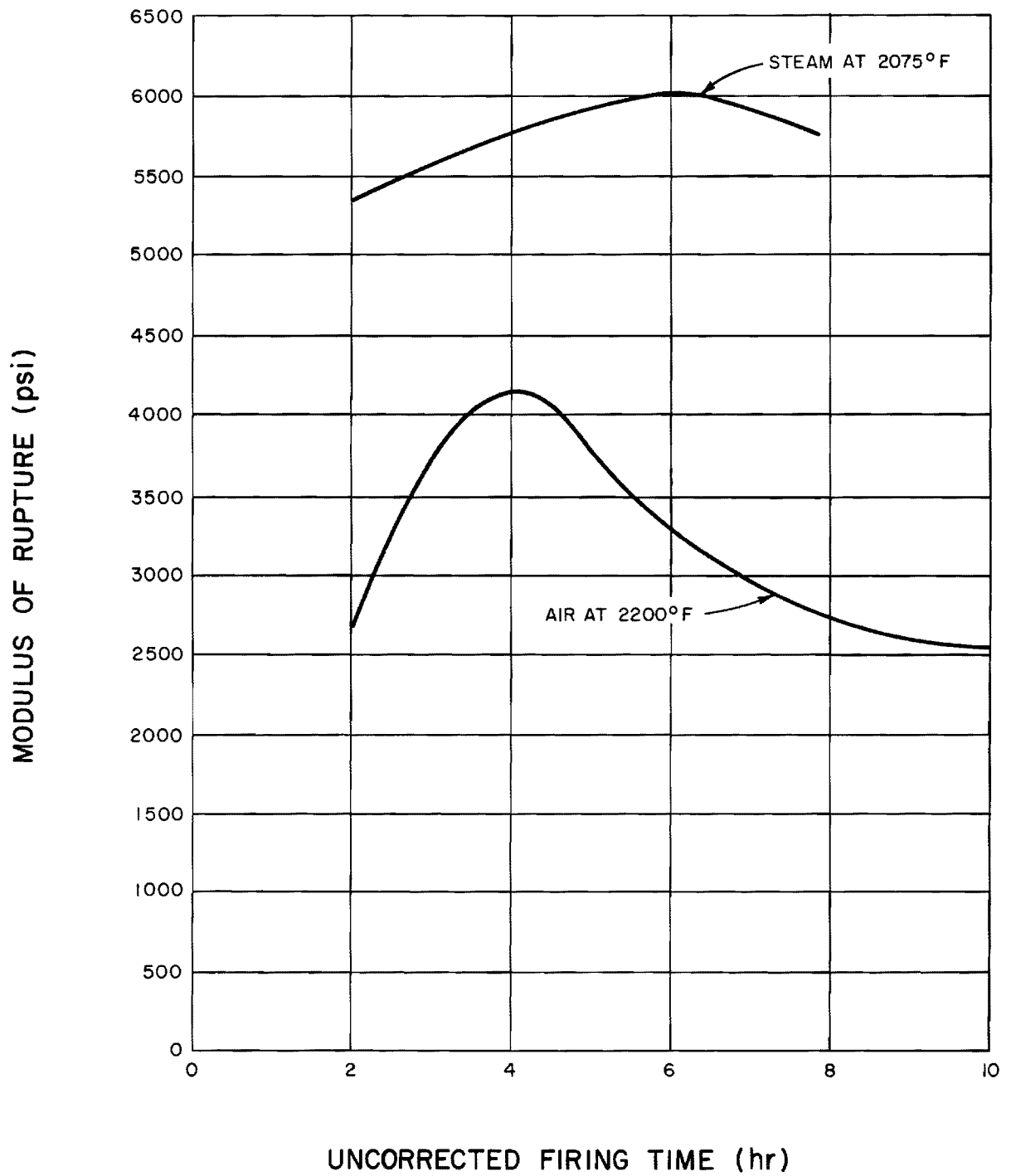


Figure 1. Comparison of Strengthening in Air Firing and Steam Firing.

was begun of an Inconel steam firing chamber for use in a large bottom loading furnace. This chamber will permit firing of larger samples and should expose the samples more uniformly. Following completion of this chamber, steam firing profile determinations will be resumed.

## 2. 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<sup>1</sup>.

The compressive strength of slip cast fused silica is shown as a function of corrected firing time<sup>2</sup> in Figure 2. The curves are quite similar in shape to the modulus of rupture profiles determined previously. The positions of the maxima differed from the peaks in the modulus of rupture and porosity curves. A comparison of these peaks, 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

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<sup>1</sup>Quarterly Report No. 1, pp. 27-29, April 1962.

<sup>2</sup>Ibid, pp. 9-15

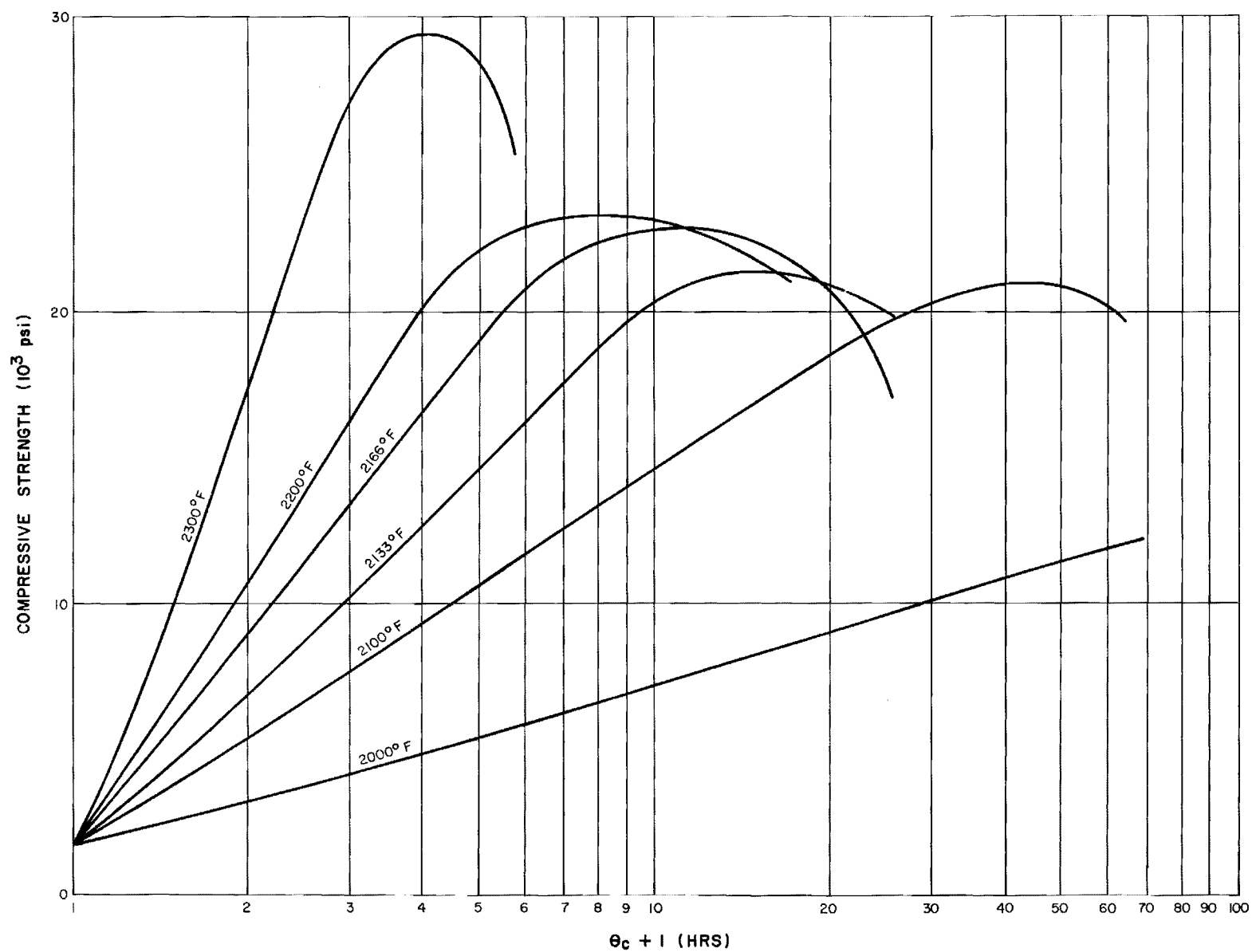


Figure 2. Compressive Strength of Slip Cast Fused Silica.



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 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 CONDITIONS FOR MAXIMUM MODULUS OF RUPTURE  
AND COMPRESSIVE STRENGTH AND MINIMUM POROSITY IN SLIP CAST FUSED SILICA

Firing Temperature (°F)	Corrected Firing Time for		
	Maximum Modulus of Rupture (hr)	Maximum Compressive Strength (hr)	Minimum Porosity (hr)
2100	49.0	47.4	46.7
2133	19.0	13.8	17.4
2166	8.5	10.0	12.4
2200	3.3	8.0	5.7
2300	1.6	3.0	2.0

### 3. Sintering Behavior

The evaluation of sintered slip cast fused silica showed that the change in bulk density could be represented by

$$\Delta B = M \ln (\theta_c + 1) \quad 1)$$

where  $\Delta B$  represents the change in bulk density (gm/cc),  $\theta_c$  is the corrected firing time (hr.) and  $M$  is a temperature dependent constant. The experimental values of  $M$  are given in Table II.

$M$  varies exponentially with the reciprocal absolute sintering temperature as shown in Figure 3. By a least squares fit of the data points in Figure 3,

$$M = \exp \left( 20.2 - \frac{62200}{T} \right). \quad 2)$$

Substituting Equation 2 into Equation 1 gives

$$\Delta B = \exp \left( 20.2 - \frac{62200}{T} \right) \ln (\theta_c + 1) \quad 3)$$

TABLE II  
SINTERING CONSTANT FOR SLIP CAST FUSED SILICA

Temperature (°F)	M	Range of Sintering Time Studied (hr)
2000	0.0056	0 - 64.2
2100	0.0165	0 - 68.3
2133	0.0226	0 - 24.4
2166	0.0326	0 - 24.4
2200	0.0404	0 - 16.4
2300	0.0877	0 - 4.79

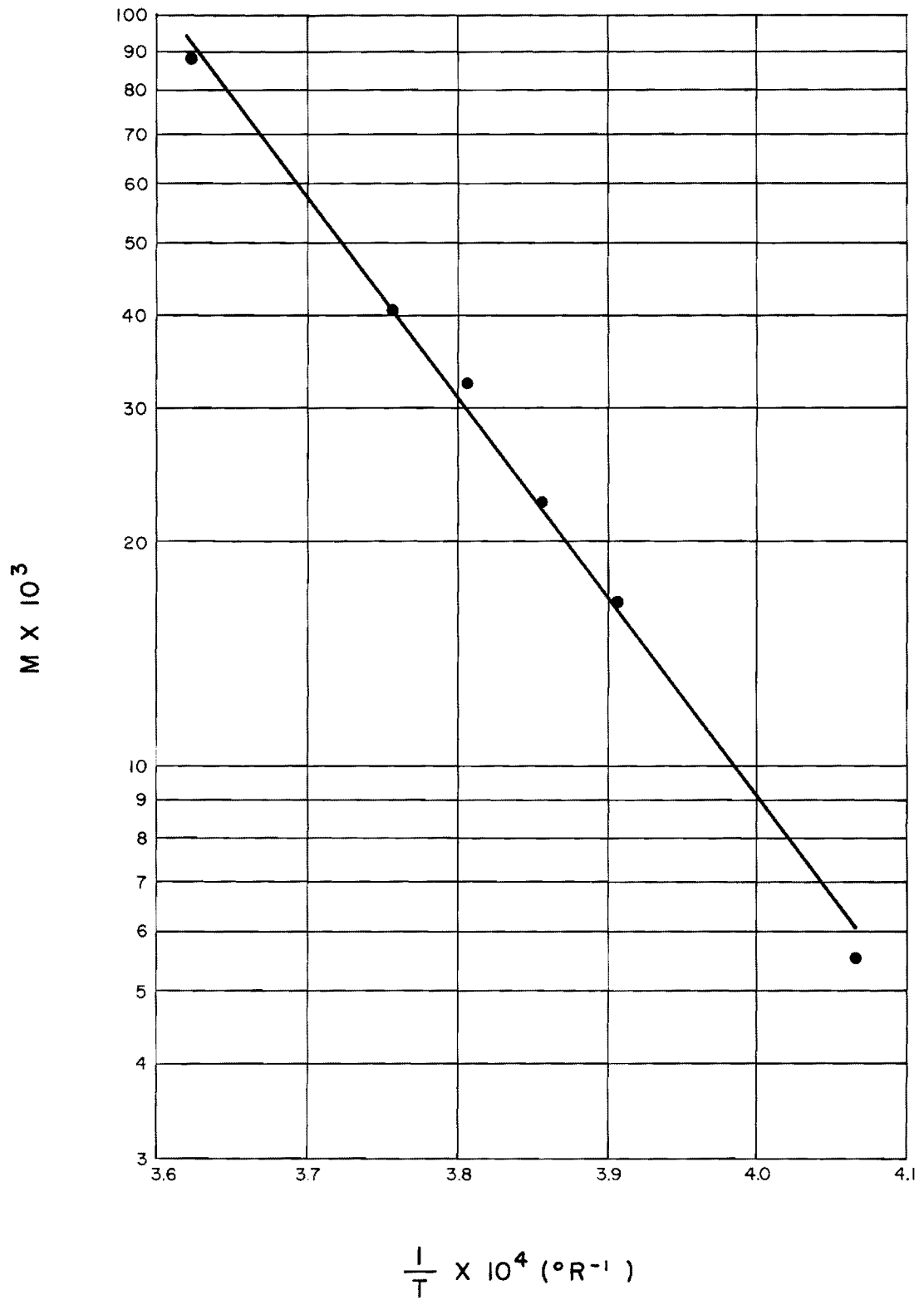


Figure 3. Sintering Constant for Slip Cast Fused Silica.

Recognition of the similarity of the bulk density equation to an Arrhenius equation prompted further investigation of the densification process in an attempt to clarify the sintering mechanism. Consideration was given to a microscopic contact point, as described in Appendix A, and the criterion of micro- and macroscopic similarity between any two test samples led to the equation

$$\frac{E}{R} = \lim_{\Delta B_1 \rightarrow 0} \frac{d(\ln \theta_1)}{d(\frac{1}{T})} \quad 4)$$

in which  $E$  is the activation energy,  $R$  is the gas constant, and  $\theta_1$  is the time required for the specified bulk density change  $\Delta B_1$ . This equation should be applicable to sintering of silica by viscous or plastic flow. For viscous flow, the slope of the plot of  $\ln \theta_1$  vs.  $1/T$  should be constant. Inasmuch as this was not the case with the silica, the data indicate that viscous flow is not the operative sintering mechanism with slip cast fused silica. Assuming that the sintering mechanism is plastic flow, application of Equation 4 to Equation 3 yields

$$E = 68.6 \frac{\text{kcal}}{\text{mole}}$$

as the activation energy for sintering of slip cast fused silica.

## B. Al-U<sub>3</sub>O<sub>8</sub> Interactions

### 1. Effect of Baymal

A brief study made earlier indicated that additions of small amounts of Baymal\* improved the uniformity of the Al-U<sub>3</sub>O<sub>8</sub> pellets but did not affect the ignition characteristics. In order to evaluate this observation more concretely,

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\* E. I. duPont hydrated colloidal alumina.

three sets of 14.6 w/o aluminum 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 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 14.6 w/o Al-U<sub>3</sub>O<sub>8</sub> COMPOSITE

<u>Baymal Additive</u> (w/o)	<u>Ignition Temperature</u> (°F)	<u>Peak Height</u> (mv)	<u>Peak Area</u> (mv-sec)
0	1650	2.20	102
0.1	1660	2.53	112
1.0	1640	2.05	79

The results were examined statistically to indicate the significance of the apparent trends as summarized in Appendix B. The averages were compared by t tests to determine the possibility that they could have been drawn from the same population. The results of these t tests are given in Table IV.

Accepting the usual 95 per cent confidence level requirement for statistical significance, the addition of 0.1 w/o Baymal failed to show a statistically significant effect on the ignition characteristics of the 14.6 w/o aluminum composite. Addition of 1 w/o Baymal significantly decreased the ignition temperature and the peak height and peak area on the DTA chart.

TABLE IV  
RESULTS OF STATISTICAL ANALYSIS OF BAYMAL ADDITIVE EFFECTS

<u>Sets of Pellets Compared</u> *	<u>Confidence Level for Significant Difference in Averages of</u>		
	<u>Ignition Temperature</u> (%)	<u>Peak Height</u> (%)	<u>Peak Area</u> (%)
0.1:0	<75	<90	<50
1.0:0	<75	>95	>99.5
1.0:0.1	>99.5	>95	>95
* Baymal contents of sets compared			

X-ray diffraction analyses of pellets containing different amounts of Baymal additive did not show any apparent differences in types or relative amounts of reaction products.

## 2. Effect of $U_3O_8$ Particle Size

In keeping with the extension of the Al- $U_3O_8$  studies to higher aluminum contents, an evaluation was made of the influence of  $U_3O_8$  particle size on the ignition characteristics of 25 w/o aluminum compacts. Spencer fused  $U_3O_8$  was separated into six particle size cuts by screening in a Syntron sieve shaker following brief milling to break up agglomerates. Pellets were pressed from mixtures of these  $U_3O_8$  fractions and Alcoa 140 atomized aluminum. Five samples from each mixture were subjected to differential thermal analysis at a heating rate of 60° F/min. The testing atmosphere was argon at 15 psig.

The ignition characteristics of these pellets are summarized in Table V.

TABLE V  
EFFECT OF  $U_3O_8$  PARTICLE SIZE  
ON IGNITION CHARACTERISTICS OF 25 w/o Al- $U_3O_8$  COMPACTS

$U_3O_8$ Particle Size (mesh)	Ignition Temperature (°F)	Peak Height (mv/gm)	Peak Area ( $\frac{mv \cdot sec}{gm}$ )
+100	1810	0.234	9.05
-100 +140	1820	0.206	5.09
-140 +200	1810	0.223	7.55
-200 +270	1840	0.209	6.33
-270 +325	1830	0.235	6.69
-325	1790	0.242	10.52

Statistical analysis was applied to the results of the differential thermal analysis tests as summarized in Appendix C. 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 higher peak areas. This would indicate more complete reactions in the -325 pellets. X-ray analysis failed to provide concrete confirmation of differences in the extent of reaction since all pellets showed complete reduction of the  $U_3O_8$  with formation of the usual products,  $\alpha-Al_2O_3$ ,  $UO_2$ ,  $UAl_2$ , and  $UAl_3$ .

The ignition characteristics were not influenced by the  $U_3O_8$  particle size in the 25 w/o pellets to the extent noted in 14.6 w/o aluminum compacts.<sup>1</sup> In the 14.6 w/o pellets, the ignition temperatures decreased from 1950 to 1790° F with decreasing particle size and the pellets showed a greater effect of particle size on peak height and peak area. The differences between the 14.6 and 25 w/o pellets are felt to arise from the considerable differences in compact structure. The 14.6 w/o pellets are only 34 v/o aluminum so that the  $U_3O_8$  is the continuous phase. During melting, the aluminum would then collect in the large pores in the +100 mesh samples, the Al- $U_3O_8$  contact would be poor, and the reaction would be expected to proceed with difficulty. In the 25 w/o pellets, the aluminum comprises 50.2 v/o of the compact and is, therefore, the continuous phase. As a result, the Al- $U_3O_8$  contact should be equally good throughout the entire particle size spectrum and relatively little difference would be expected in the ignition characteristics. In effect, the 14.6 w/o pellets should be affected by decreasing particle size both from increased contact through better Al- $U_3O_8$  particle size matching and from an increase in the reactive surface area. In the 25 w/o pellets, only an increase in reactive surface area would be expected, leading to somewhat less marked particle size influence. The data support these qualitative observations.

Weight changes were monitored as carefully as possible in the 25 w/o pellets. This proved difficult because some material was frequently lost through sticking to the alumina spaghetti and the results showed a great degree of variability. The results are summarized in Table VI.

The weight changes were subjected to statistical analysis as summarized in Appendix C. Only the -200 +270  $U_3O_8$  particle size pellets showed weight losses

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<sup>1</sup>Summary Report No. 1, p. 40 (June 1962).



significantly different from the other pellets. Cursory examination of the data indicates this to be a random effect.

In most cases, pellets giving greater peak heights showed the largest weight changes. The pellets with finer  $U_3O_8$  particle sizes tended to show smaller weight losses. Only in one pellet was an apparent weight gain recorded. The weight loss was less than 10 per cent in all pellets.

Metallography was begun to compare the reacted pellets.

TABLE VI  
WEIGHT CHANGES IN 25 w/o Al- $U_3O_8$  COMPACTS DURING IGNITION

<u><math>U_3O_8</math> Particle Size</u>	<u>Weight Loss</u>
(mesh)	(%)
+100	4.45
-100 +140	4.12
-140 +200	5.30
-200 +270	0.59
-270 +325	0.96
-325	3.46

### 3. High Aluminum Composites

Past studies of composites containing more than about 40 w/o aluminum failed to show definite reaction temperatures on differential thermal analysis. 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.

Several agencies interested in Al-U<sub>3</sub>O<sub>8</sub> dispersion fuels requested that the differential thermal analysis system be increased in sensitivity and that a brief survey be made of composites in the range of 50-65 w/o aluminum. This modification in the program was approved by the sponsor and efforts were begun to complete the survey as rapidly as possible.

In the investigations of low aluminum 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 high aluminum composites. 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 25 w/o aluminum pellets was pressed using "dead-burned" Y-12 U<sub>3</sub>O<sub>8</sub> supplied by the Metals and Ceramics Division, Oak Ridge National Laboratory. The 25 w/o 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.<sup>1</sup> The system sensitivity seemed to be roughly an order of magnitude greater than before modification.

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<sup>1</sup>Further studies are planned for the near future to provide statistical comparisons of ignition in pellets with Y-12 and Spencer Fused U<sub>3</sub>O<sub>8</sub>.

Several 50 w/o aluminum 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. The DTA curve fluctuated wildly during heating but the aluminum melting point and 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 v/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. 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 begun to select a better standard than the pressed alumina. These studies are not yet complete but, so far, a satisfactory standard has not been found. The results from all standards have been similar to the DTA chart shown in Figure 4. This chart was obtained using an Al-Al<sub>2</sub>O<sub>3</sub> standard containing the same volume per cent of Al<sub>2</sub>O<sub>3</sub> as the U<sub>3</sub>O<sub>8</sub> in the unknown. The exotherm at 1760° F appears sharp enough to warrant the conclusion that a reaction occurred. Certainly the lower temperature behavior is too obscure for comment. All standards used to date have indicated reactions in the range of 1700-1840° F but none has clearly defined the low temperature behavior.

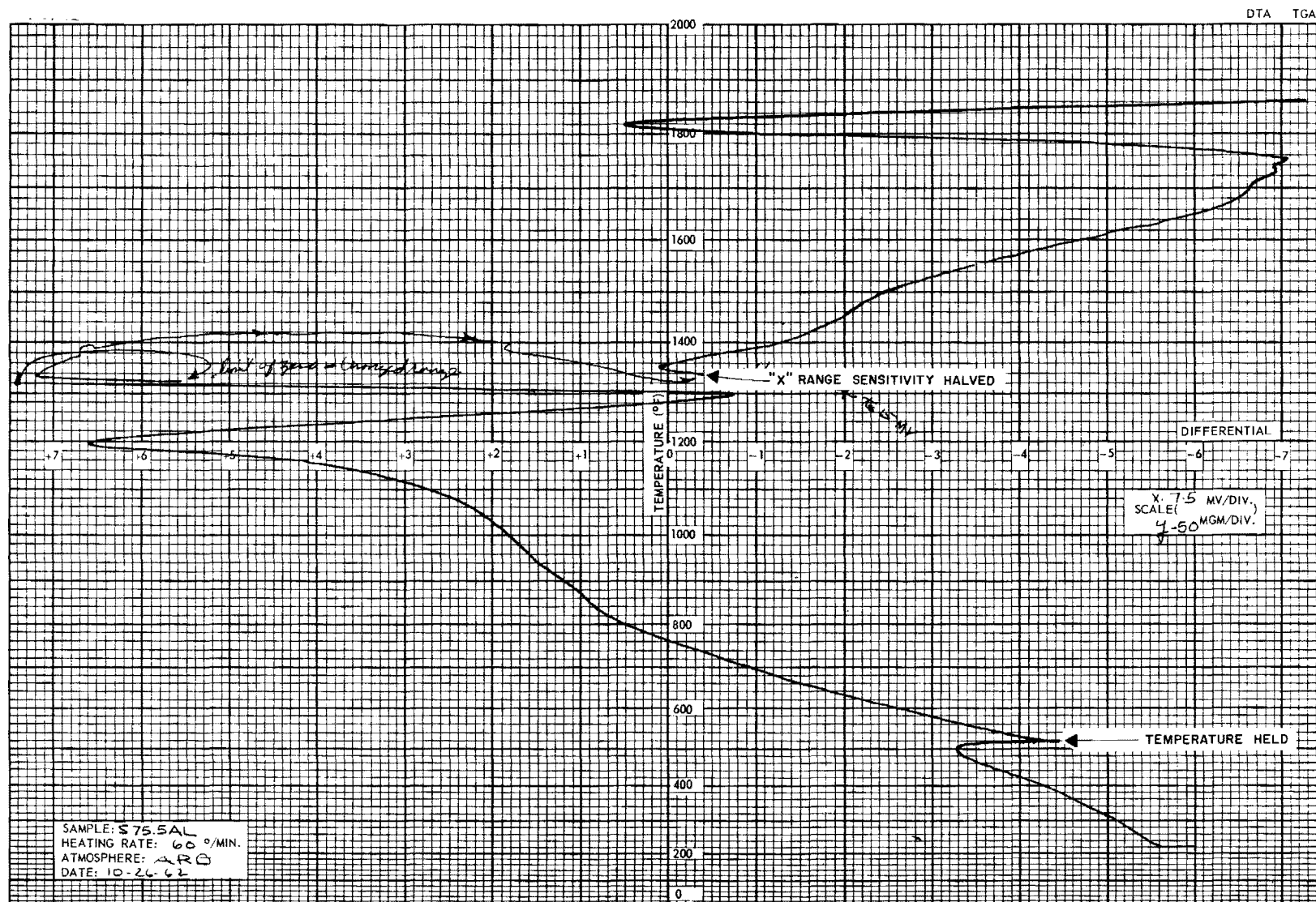


Figure 4. DTA Chart from 50 w/o Al-U<sub>3</sub>O<sub>8</sub> Composite.

#### IV. DISCUSSION

The steam firing studies continued to show promise of providing improved processing techniques and increased strength. The tube furnace used for the firings produced sufficiently prominent thermal gradients and variations in steam flow to mask systematic effects of steam firing. The steam firing chamber now being constructed will permit larger sample numbers to be fired, providing a better basis for statistical analysis, and should yield more uniform firing conditions.

The contact point analysis applied to the sintering of slip cast fused silica yielded very interesting results. The fact that the data followed the predicted behavior for plastic flow does not confirm this as the sintering mechanism for slip cast fused silica. Any process which is geometry dependent and which shows a rate constant following an Arrhenius variation with temperature will probably be resolved by a similar treatment. Further attention will be given to this approach in the future with respect to different geometries and different mass transport mechanisms. This treatment will also be applied to steam firing of the silica to provide activation energy comparisons.

In view of the rather unexpected effects of Baymal additives on the ignition behavior of  $\text{Al-U}_3\text{O}_8$  composites, no more than 0.1 w/o will be used in future studies. The results indicate that a more detailed evaluation of the effects of Baymal should be made. Such an investigation will be begun as soon as time permits.

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The studies of high aluminum composites have indicated reactions in 50 w/o aluminum pellets at temperatures in the range of 1700-1840° F. Since the standards have been far from satisfactory in providing clean DTA curves, considerable caution is necessary in stating the significance of the results. Further investigations may indicate that reactions can be confirmed only by comparison of DTA curves from fired and unfired compacts.

While the results of the studies of high aluminum composites are of considerable interest, it now appears certain that this brief study will not resolve questions as to the safety implications of the Al-U<sub>3</sub>O<sub>8</sub> reactions. The lack of a suitable standard means that differential thermal analysis will not prove capable of indicating the presence or absence of low temperature reactions. Unless future results imply a better approach, the study of the high aluminum compacts will be confined to:

- A. Selection of the most suitable standard following brief evaluations.
- B. Differential thermal analysis of Al-U<sub>3</sub>O<sub>8</sub> composites containing 50, 55, 60, and 65 w/o aluminum.
- C. Differential thermal analysis of pellets cut from a rolled Al-U<sub>3</sub>O<sub>8</sub> plate, containing about 65 w/o aluminum, to be fabricated by ORNL.
- D. Metallographic and x-ray examination of samples from B and C above.

These studies will be kept as brief as possible and will not constitute a thorough investigation.

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. S. H. Bomar	Group Leader
Mr. A. R. Colcord	Group Leader
Mr. N. K. Hearn	Assistant Research Physicist
Mr. R. K. Butz	Technician
Mr. P. A. Darius	Technician
Mr. A.C. Evans	Technician
Mr. W. M. Linstrom	Technician
Mr. P. S. Matrangos	Technician
Mr. G. W. Smith	Technician

Submitted by:

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Approved:

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Quarterly Report No. 2, Project No. B-153

VI. APPENDICES



APPENDIX A

Sintering by Viscous Flow

Useful information may be gained from consideration of a microscopic contact, of any selected geometry, which would be statistically reproduced in every member of a series of slip cast bars formed from random fracture particles. Taking the model of Clark and White<sup>1</sup> for convenience, the case of spherical contact points, shown in Figure 5 was treated.

The lens ABCD is assumed to grow by viscous flow of material across the similar planes AB and CD. The flow across the plane AB may be represented by the Bingham equation

$$\frac{du_r}{dr} = \frac{1}{\eta_{\infty}} (S_r - S') \quad 1)$$

where  $u_r$  is the velocity perpendicular to the plane AB at the radial position  $r$ ,  $\eta_{\infty}$  is the coefficient of viscosity at infinite shear rate,  $S_r$  is the applied shearing stress and  $S'$  is the effective yield stress. The applied stress is assumed to result from the excess surface energy or surface tension attempting to minimize the free surface by growth of the lens ABCD. This applied stress will then be a function of the surface tension and the free surface area or the geometric parameters  $r_t$ ,  $R_i$ , and  $r$ .

In functional notation

$$S_r = F_1 (\gamma, R_i, r_t, r). \quad 2)$$

Substituting Equation 2 in Equation 1 yields

$$\frac{du_r}{dr} = \frac{1}{\eta_{\infty}} [F_1 (\gamma, R_i, r_t, r) - S']$$

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<sup>1</sup>Clark, P. W. and J. White, Trans. Brit. Ceram. Soc. 49 305-33 (1950).

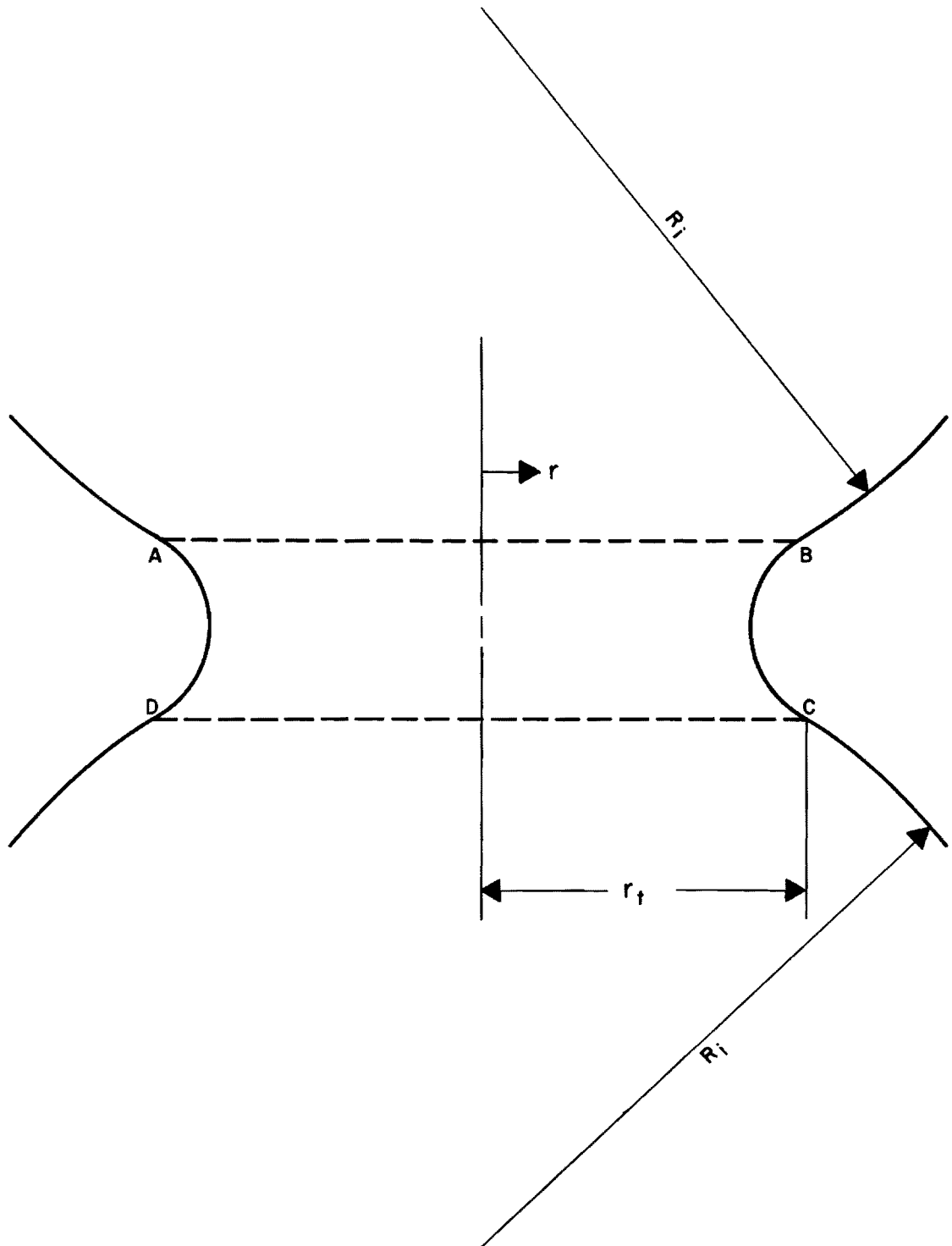


Figure 5. Spherical Contact Point between Fused Silica Particles.

which, upon integration, gives

$$u_r = \frac{1}{\eta_{\infty}} [F_2 (\gamma, R_i, r_t, r) - S'r]. \quad (3)$$

The volumetric flow rate across the plane AB is

$$\frac{dV}{d\theta} = \int_0^{r_t} 2\pi r u_r dr. \quad (4)$$

Substituting Equation 3 into Equation 4 and integrating

$$\frac{dV}{d\theta} = \frac{1}{\eta_{\infty}} [F_3 (\gamma, R_i, r_t) - S' F_4 (r_t)] \quad (5)$$

Since the same volumetric flow rate will occur across the plane CD, the rate of change of the lens volume is

$$\frac{dV_l}{d\theta} = 2 \frac{dV}{d\theta}. \quad (6)$$

If  $R_i$  is taken as a constant,  $r_t$  will be defined by the lens volume. Assuming  $\gamma$  to be constant,

$$F_3 (\gamma, R_i, r_t) = F_5 (V_l) \quad (7)$$

and

$$F_4 (r_t) = F_6 (V_l). \quad (8)$$

From the Eyring kinetic theory for fluids

$$\eta_{\infty} = \frac{\sigma}{a} \frac{Nh}{V} e^{E/RT} \quad (9)$$

where  $\frac{\sigma}{a}$  is normally taken as unity, N is avagadro's number, h is Planck's constant, V is the molal volume, E is the activation energy, R is the gas constant, and T is the absolute temperature. Since the thermal expansion coefficient of fused silica is very low, V is essentially constant and

$$\eta_{\infty} \doteq Ae^{\frac{E}{RT}} \quad 10)$$

Substituting Equations 6, 7, 8, and 10 into Equation 5 gives

$$\frac{dV_{\ell}}{d\theta} \doteq Ae^{\frac{E}{RT}} [F_5(V_{\ell}) - S' F_6(V_{\ell})]. \quad 11)$$

If the flow process is Newtonian, the yield stress is zero and

$$\frac{dV_{\ell}}{F_5(V_{\ell})} \doteq Ae^{-\frac{E}{RT}} d\theta. \quad 12)$$

Equation 12 may be integrated to yield

$$\int_0^{V_{\ell_i}} \frac{dV_{\ell}}{F_5(V_{\ell})} \doteq Ae^{-\frac{E}{RT}} \theta_i. \quad 13)$$

If  $V_{\ell_i}$  is set at a given arbitrary lens volume and  $\theta_i$  is the time to reach that volume, the left side of Equation 13 is a constant and

$$\ln \theta_i \doteq \ln A' + \frac{E}{RT} \quad 14)$$

A plot of the log of the time to reach the given lens volume as a function of reciprocal temperature should then be represented by a straight line, according to Equation 14. The slope of the line should be

$$\frac{d(\ln\theta_i)}{d(1/T)} = \frac{E}{R} \quad 15)$$

If the flow is non-Newtonian, the yield stress is not zero but, for short sintering times, the applied stress should be much greater than the yield stress.<sup>1</sup> As a result, Equation 12 still holds at the limit  $V_l \rightarrow 0$ , and

$$\lim_{V_l \rightarrow 0} \frac{d(\ln\theta_i)}{d(1/T)} = \frac{E}{R} \quad 16)$$

In applying these results in practice, a modification is desirable since examination of a contact point such as shown in Figure 5 is obviously impractical. In most sintering experiments, the test specimens are all assumed to be identical. If a contact point, such as that of Figure 5, exists in any bar, as it must if the bar is composed of a very large number of random fracture particles, then such a point must occur at least once in any specimen of an identical set. In addition, if the bars are identical, the behavior of the contact points in all the bars must be exactly the same during sintering. If the bulk density change in one bar is  $\Delta B_i$  when the contact point lens volume is  $V_{l_i}$ , then the same must be true of all other bars in the sample population. In this manner, the bulk density change,  $\Delta B$ , must be a linear index of the contact point lens volume even if the exact relating equation is not known. As a result, if  $V_{l_i}$  in Equation 13 is defined as the lens volume when the bulk density change is  $\Delta B_i$ ,  $\theta_i$  becomes the time when the bulk density change is  $\Delta B_i$ , and Equation 14 may be represented by a plot of the log of the time to reach  $\Delta B_i$  vs the reciprocal sintering temperature. Equation 15 need not be modified for such a plot. Equation 16 becomes simply

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<sup>1</sup>Clark, P. W., J. H. Cannon, and J. White, Trans. Brit. Ceram. Soc. 52 1-49 (1953).

$$\lim_{\Delta B_i \rightarrow 0} \frac{d(\ln \theta_i)}{d(1/T)} = \frac{E}{R} \quad 17)$$

The bulk density changes on sintering, which can be measured easily, may now be used as indices for the calculation of the activation energy.

APPENDIX B

Statistical Analysis of Baymal Study

In order to examine the influence of Baymal additives on the ignition characteristics of  $\text{Al-U}_3\text{O}_8$  composites, statistical analysis was applied to the data, summarized in Table VII. The averages were compared by Student t tests<sup>1</sup> which are summarized in Table VIII.

TABLE VII

SUMMARY OF BAYMAL STUDY RESULTS

<u>Variable</u>	<u>Baymal Content (w/o)</u>	<u>Number of Samples (n)</u>	<u>Mean (m)</u>	<u>Variance Estimate (<math>s^2</math>)</u>
Ignition Temperature	0	2	1655° F	450.0000
	0.1	4	1663° F	8.3333
	1.0	4	1644° F	6.2500
Peak Height	0	2	2.20 mv	0
	0.1	4	2.53 mv	0.049167
	1.0	4	2.05 mv	0.003333
Peak Area	0	2	101.8 mv-sec	15.1250
	0.1	4	112.2 mv-sec	661.2336
	1.0	4	79.4 mv-sec	13.7656

<sup>1</sup>Volk, William, "Applied Statistics for Engineers", pp. 115-121, McGraw-Hill Book Company, Inc., New York (1958).

TABLE VIII  
SUMMARY OF t TESTS OF BAYMAL STUDY RESULTS<sup>+</sup>

Variable	Baymal Contents Compared	Pooled Standard Deviation	t
Ignition Temperature	1.0:0	10.8250	-1.1947
	0.1:0	10.8974	0.7947
	1.0:0.1	2.7003	-9.7940***
Peak Height	1.0:0	0.05000	-3.4642*
	0.1:0	0.19203	1.9844
	1.0:0.1	0.162014	-4.1903**
Peak Area	1.0:0	3.7557	-6.8869***
	0.1:0	22.3500	0.5382
	1.0:0.1	18.3712	-2.5096

<sup>+</sup>Note: Significance designated by asterisks on t value.

\*  $\equiv$  > 95% confidence level

\*\*  $\equiv$  > 99% confidence level

\*\*\*  $\equiv$  > 99.5% confidence level

The t tests summarized in Table VIII failed to show any effect on ignition characteristics with Baymal additions of 0.1 w/o. Addition of 1.0 w/o Baymal lowered the ignition temperature, presumably through better mixing, and decreased the differential thermal analysis peak height and peak area.



APPENDIX C

Statistical Analysis of  $U_3O_8$  Particle Size Study

The ignition characteristics of the pellets with different particle size  $U_3O_8$  were compared by single factor variance analysis. The data are summarized in Table IX and the variance analyses<sup>1</sup> are summarized in Table X.

TABLE IX

SUMMARY OF  $U_3O_8$  PARTICLE SIZE STUDY RESULTS

Variable	$U_3O_8$ Mesh Size	Number of Samples (n)	Mean (m)	Variance Estimate ( $s^2$ )
Ignition Temperature	+100	5	1807° F	95.0000
	-100 +140	4	1820° F	266.6667
	-140 +200	5	1814° F	430.0000
	-200 +270	5	1838° F	1270.0000
	-270 +325	5	1828° F	170.0000
	-325	3	1787° F	233.3333
Peak Height	+100	5	0.2340 mv	0.0002325
	-100 +140	4	0.2055 mv	0.0005643
	-140 +200	5	0.2225 mv	0.0016133
	-200 +270	5	0.2085 mv	0.0056530
	-270 +325	5	0.2348 mv	0.0004814
	-325	5	0.2419 mv	0.0014536

(Continued)

<sup>1</sup>For calculation methods see Volk, William, "Applied Statistics for Engineers", pp. 158-178, McGraw-Hill Book Co., New York (1958).

TABLE IX (Continued)

SUMMARY OF  $U_3O_8$  PARTICLE SIZE STUDY RESULTS

Variable	$U_3O_8$ Mesh Size	Number of Samples (n)	Mean (m)	Variance Estimate ( $s^2$ )
Peak Area	+100	5	0.1086 in <sup>2</sup>	0.0000493
	-100 +140	4	0.0611 in <sup>2</sup>	0.0008066
	-140 +200	5	0.0906 in <sup>2</sup>	0.0001151
	-200 +270	5	0.0760 in <sup>2</sup>	0.0022159
	-270 +325	5	0.0803 in <sup>2</sup>	0.0000848
	-325	5	0.1262 in <sup>2</sup>	0.0006302
Weight Loss	+100	5	4.452 %	6.1031
	-100 +140	4	4.124 %	17.8991
	-140 +200	5	5.298 %	14.0779
	-200 +270	5	0.590 %	0.6758
	-270 +325	5	0.958 %	0.4335
	-325	5	3.456 %	4.8102

TABLE X

SUMMARY OF VARIANCE ANALYSIS OF  $U_3O_8$  PARTICLE SIZE STUDY

IGNITION TEMPERATURE

a. All groups:

<u>Source</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Within Groups	9,127	21	434.6
Between Groups	6,142	5	1228.4
Total	15,269	26	

$$F \frac{\text{Between}}{\text{Within}} = 2.8265$$

$$F_{5/21, 0.05} = 2.6848$$

b. Omitting -325 group:

<u>Source</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Within Groups	8,660	19	455.8
Between Groups	2,914	4	728.5
Total	11,574	23	

$$F \frac{\text{Between}}{\text{Within}} = 1.5983$$

$$F_{4/19, 0.1} = 2.2663$$

(Continued)

TABLE X (Continued)

SUMMARY OF VARIANCE ANALYSIS OF  $U_3O_8$  PARTICLE SIZE STUDY

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<u>PEAK HEIGHT</u>			
a. <u>All groups:</u>			
<u>Source</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Within Groups	0.039428	23	0.0017143
Between Groups	0.005217	5	0.0010434
Total	0.044645	28	
$F \frac{\text{Between}}{\text{Within}} = 0.6086$			
$F_{5/32, 0.5} = 0.8964$			

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<u>PEAK AREA</u>			
a. <u>All groups:</u>			
<u>Source</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Within Groups	0.014800	23	0.00064351
Between Groups	0.013102	5	0.00262042
Total	0.027902	28	
$F \frac{\text{Between}}{\text{Within}} = 4.0721$			
$F_{5/23, 0.01} = 3.9392$			

---

(Continued)

TABLE X (Continued)

SUMMARY OF VARIANCE ANALYSIS OF  $U_3O_8$  PARTICLE SIZE STUDY

b. Omitting -325 group:

<u>Source</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Within Groups	0.012280	19	0.0006463
Between Groups	0.005818	4	0.0014546
Total	0.018099	23	
$F \frac{\text{Between}}{\text{Within}} = 2.2506$			
$F_{4/19, 0.10} = 2.2663$			

WEIGHT LOSS

a. All groups:

<u>Source</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Within Groups	158.099	23	6.8738
Between Groups	104.568	5	20.9135
Total	262.667	28	
$F \frac{\text{Between}}{\text{Within}} = 3.0425$			
$F_{5/23, 0.05} = 2.6400$			

(Continued)

TABLE X (Continued)

SUMMARY OF VARIANCE ANALYSIS OF  $U_3O_8$  PARTICLE SIZE STUDY

b. Omitting -200+270 group:

<u>Source</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Within Groups	155.396	19	8.1787
Between Groups	61.664	4	15.4160
Total	217.060	23	

$$F \frac{\text{Between}}{\text{Within}} = 1.8849$$

$$F_{4/19, 0.10} = 2.2663$$

t Tests

a. Ignition Temperature

$$-325 \text{ mean} = 1787^\circ \text{ F, } n = 3$$

$$+325^* \text{ mean} = 1821^\circ \text{ F, } n = 24$$

$$\text{Pooled standard deviation} = 20.847$$

$$t = 2.6633$$

$$t_{25, 0.025} = 2.3846$$

$$t_{25, 0.01} = 2.7874$$

(Continued)

TABLE X (Continued)

SUMMARY OF VARIANCE ANALYSIS OF  $U_3O_8$  PARTICLE SIZE STUDY

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b. Peak Area

-325 mean = 0.12618, n = 5

+325<sup>\*</sup> mean = 0.08422, n = 24

Pooled standard deviation = 0.025367

t = 3.3649

$t_{27,0.005}$  = 3.0565

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\* Pooled value of all +325 groups.

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The variance analysis and t tests indicated that -325 mesh  $U_3O_8$  produced significantly lower ignition temperatures and higher peak area. Above -325 mesh  $U_3O_8$ , there was no statistically significant effect of  $U_3O_8$  particle size.

The -200+270 mesh group showed a significantly lower weight loss during ignition. This is felt to be a random, rather than systematic, effect.

VII. PRIOR REPORTS

Previous reports issued under this contract are:

1. Monthly Letter Reports Nos. 1 - 46. Issued each month since December 1958.
2. Progress Report No. 1, August 1959. Issued as ORO-209 by OTS, Department of Commerce.
3. Progress Report No. 2, Part 1, August 1960. Issued as ORO-325 by OTS, Department of Commerce.
4. Progress Report No. 2, Part 2 (Declassified), August 1960.
5. Progress Report No. 3, August 1961.
6. Quarterly Report No. 1, April 1962.
7. Summary Report No. 1, July 1962.



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QUARTERLY REPORT NO. 3

PROJECT NO. B-153

MATERIALS FOR HIGH TEMPERATURE  
NUCLEAR ENGINEERING APPLICATIONS

By J. D. Fleming, J. W. Johnson,  
Paul Boland, and S. H. Bomar

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

Contract No. AT-(40-1)-2483

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1963



Engineering Experiment Station  
**GEORGIA INSTITUTE OF TECHNOLOGY**  
Atlanta, Georgia

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

QUARTERLY REPORT NO. 3  
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By

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

OCTOBER 1, 1962 to JANUARY 1, 1963

Quarterly Report No. 3, Project No. B-153

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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.

This report covers the period from October 1, 1962 to January 1, 1963.

## Quarterly Report No. 3, Project No. B-153

### 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



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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  $U_3O_8$ . Since Al- $U_3O_8$  dispersions are in common use as reactor fuels, the results of this study are obviously of interest in hazards evaluation. Several special studies of Al- $U_3O_8$  dispersions are included in the program to assist hazards evaluation.

## II. SUMMARY

A statistical study was made to determine the effects of the time allowed for thermal equilibration in the high temperature ring tensile test of slip cast fused silica. The study consisted of three firings with the rings from each being broken at 2000° F after soaking times ranging from three minutes to approximately 35 minutes. The statistical analysis of the breaking loads showed variations between firings at greater than the 99 per cent confidence level. Variations between soaking times failed to show significance at the 95 per cent confidence level. No evidence was detected of an interaction between the two factors.

Studies were made of steam sintering slip cast fused silica at 2000, 2100, and 2200° F with a controlled steam flow rate of 0.72 pounds per hour. The strengthening profiles as a function of firing time and temperature indicated a sintering mechanism similar to that in air firing but much more rapid sintering kinetics. At 2100° F in steam firing, a peak modulus of rupture of 4500 psi was reached in 8-1/2 hours while in air firing the peak strength of 4200 psi was reached in 49 hours. In air firing, the minimum porosity attained was 14.2 per cent after which an increase was noted. In steam firing, the lowest porosity reached was 12.6 per cent but no indication was given that the porosity was reaching a minimum. The bulk density increased linearly with time in steam firing, indicating that the sintering mechanism is viscous flow. The bulk density changes followed the equation

$$B = 1.854 + \exp \left( 33.5 - \frac{99300}{T} \right) \theta$$

where B is the bulk density (gm/cc), T is the absolute sintering temperature (°R) and  $\theta$  is the sintering time (hr.). From this equation, an activation energy

of 110 kcal per mole was calculated for steam firing of slip cast fused silica at a steam flow rate of 0.72 pounds per hour.

Studies were begun of  $\text{Al-U}_3\text{O}_8$  reactions in a rolled plate of ATR composition, containing 33.79 w/o  $\text{U}_3\text{O}_8$ , 66.07 w/o X-800 aluminum and 0.14 w/o  $\text{B}_4\text{C}$ . Differential thermal analysis curves from specimens of this plate did not differ significantly from curves obtained with cold pressed pellets of similar composition. A small exotherm was noted, peaking at approximately 1300° F. Immediately following the exotherm, a very large aluminum melting endotherm appeared. A second exotherm peaked at 1820-1840° F. During this exotherm, the unknown pellet appeared visually to glow slightly brighter than the standard. Upon cooling, an aluminum solidification exotherm was noted but its size was somewhat smaller than the melting endotherm. The difference in size of the two peaks increased with increasing pellet firing temperature.

Plate ATR specimens were subjected to x-ray diffraction in the as-received condition, after vacuum annealing, and after being heated to 1000, 1200, 1400, 1600, and 1830° F at 60° F per minute. Both aluminum and  $\text{U}_3\text{O}_8$  showed consistent decreases with increasing severity of heating. The  $\text{UO}_2$  peaks were largest in the vacuum annealed sample although they appeared in all samples.  $\text{Al}_2\text{O}_3$  peaks first appeared in the 1000° F specimen and increased consistently in intensity with increasing heating temperature.  $\text{UAl}_4$  was detected in small amounts in the 1000° F specimen but not again until the 1600° F specimen. In the 1600° F specimen, small amounts of  $\text{UAl}_3$  and  $\text{UAl}_4$  appeared. The  $\text{UAl}_3$  and  $\text{UAl}_4$  peaks were well defined in the 1830° F specimen although residual  $\text{U}_3\text{O}_8$  was still present. These results support the suggestion of a probable two stage reaction with initial reduction of  $\text{U}_3\text{O}_8$  to  $\text{UO}_2$  followed by further reduction to  $\text{UAl}_3$  and  $\text{UAl}_4$ . Complete reduction of the  $\text{U}_3\text{O}_8$  to  $\text{UO}_2$  prior to  $\text{UAl}_3$  and  $\text{UAl}_4$  formation did not occur.

Preliminary metallographic examination of the ATR specimens indicated formation of a reaction zone, probably principally  $\text{Al}_2\text{O}_3$ , around the  $\text{U}_3\text{O}_8$  particles which were converted to a fragmented structure. Gas pores and grain boundary precipitation, presumably  $\text{UAl}_4$ , were noted, increasing significantly in concentration with increasing heating temperature.

Initial studies were made to compare reactions in cold pressed Al- $\text{UO}_2$  pellets with those in cold pressed Al- $\text{U}_3\text{O}_8$  pellets. DTA curves from the two systems were quite similar in appearance. The reaction exotherm in Al- $\text{UO}_2$  occurred at  $1820^\circ\text{F}$  compared with  $1780^\circ\text{F}$  for Al- $\text{U}_3\text{O}_8$ . The reaction in Al- $\text{UO}_2$  appeared more energetic although insufficient samples were tested to permit statistical comparison.

### III. EXPERIMENTAL WORK

#### A. Slip Cast Fused Silica

##### 1. High Temperature Tensile Strength

In preparation for the last series of high temperature ring tensile tests, a series of tests was made to determine the influence of the time for thermal equilibration allowed following insertion of the sample into the testing furnace. A set of 36 fused silica rings was cast using Keltex mold release. The rings were fired in groups of 12 at 2200° F for an uncorrected firing time of two hours. During firing, the rings rested on an Alundum plate and were shielded with Inconel sheeting.

The fired rings were broken in the ring tester at 2000° F. Four rings from each firing were broken as soon as possible, approximately three minutes, after insertion into the testing furnace, four after return of the furnace to the testing temperature of 2000° F, and four five minutes after the furnace returned to 2000° F. The experiment was programmed to avoid bias due to testing sequence and specimen placement during firing.

The results of the tensile tests are summarized in Appendix A. Since the dimensions of the rings did not vary significantly, statistical analysis was applied directly to the breaking loads rather than to computed tensile strengths. A two factor analysis of variance was used to examine the effects of re-heat time, firing to firing variation, and the second order interaction between the two. The results of this analysis are summarized in Table I.

The firing to firing variation proved significant at better than the 99 per cent confidence level. This is in agreement with prior work and appears unavoidable without extensive equipment redesign and more than reasonable precision in firing procedure.

TABLE I  
ANALYSIS OF VARIANCE OF RING TEST DATA

<u>Source of Estimate</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square Estimate</u>	<u>F</u>
Between Firings	207,239	2	103,620	6.36***
Between Re-heats	100,643	2	50,322	3.09
Interactions	150,535	4	37,634	2.31
Error	440,201	27	16,304	-

$F_{0.05, 2/27} = 3.35$	$F_{0.05, 4/27} = 2.73$
$F_{0.01, 2/27} = 5.49$	*** Significant at >99 per cent level of confidence.
$F_{0.005, 2/27} = 6.49$	

The time allowed for reheating prior to testing failed to show significance at the 95 per cent level of confidence required for statistical validity. This is not surprising since the point of maximum stress in the ring is at an exposed surface and a rapid thermal equilibration at this point would be expected. In order to provide a uniform basis for future testing, the ring furnace will be allowed to return to the testing temperature prior to load application.

## 2. Steam Firing

Studies made during the previous quarter indicated that firing the slip cast fused silica in a steam atmosphere failed to give reproducible results when a tube furnace was used. Prior to accepting the expense of building an Inconel chamber for steam firing in the bottom loading furnace, however, an attempt was made to improve the results by modifying the steam flow system. In order to achieve this, a ballast tank was inserted into the water flow line. The air space

over the water in the ballast tank was pressurized and held at a constant pressure by means of a compressed air regulator. The water flow was then adjusted by means of a rotameter and water was introduced directly into the furnace tube.

In order to check the modified flow system, a group of 264 fused silica bars, 3/4-inch in diameter and 5-5/8-inches long, was cast in one piece molds using the graphite mold release. The bars were fired in sets of 11 in the tube furnace. The firing conditions were 2000° F for<sup>1</sup> 6-1/4, 24, 40, 66, and 68 hours, 2100° F for 1, 2, 4, 8, and 16 hours and 2200° F for 1, 2, and 4 hours. Two sets were fired at each combination of firing temperature and time except for the 2000° F runs for 66 and 68 hours in which only one set was used at each point. In all runs, the water flow rate was 0.72 pounds per hour.

The porosity, bulk density, and apparent theoretical density of each fired bar were determined using the air displacement porosimeter. Following these measurements, the bars were tested for modulus of rupture in three point loading on a Tinius-Olsen Super L universal tester. Each bar was broken on a four inch span and twice on a two inch span using the halves from the first break.

The modulus of rupture of the steam fired bars is shown in Figure 1 which indicates that the strengthening process is qualitatively similar in steam and air firing. Initial strengthening occurs with improved sintering until post-firing cooling produces micro-flaws in the interfacial cristobalite. While the strengthening mechanism is apparently similar in air and steam firing, the kinetics are quite different. As an illustration of this, the 2100° F firing profiles for air and steam are compared in Figure 2.

In Figure 3, the porosity profiles are shown for steam firing. Again, a significant difference from air firing is noted. While in air firing a minimum

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<sup>1</sup>All firing times are uncorrected.

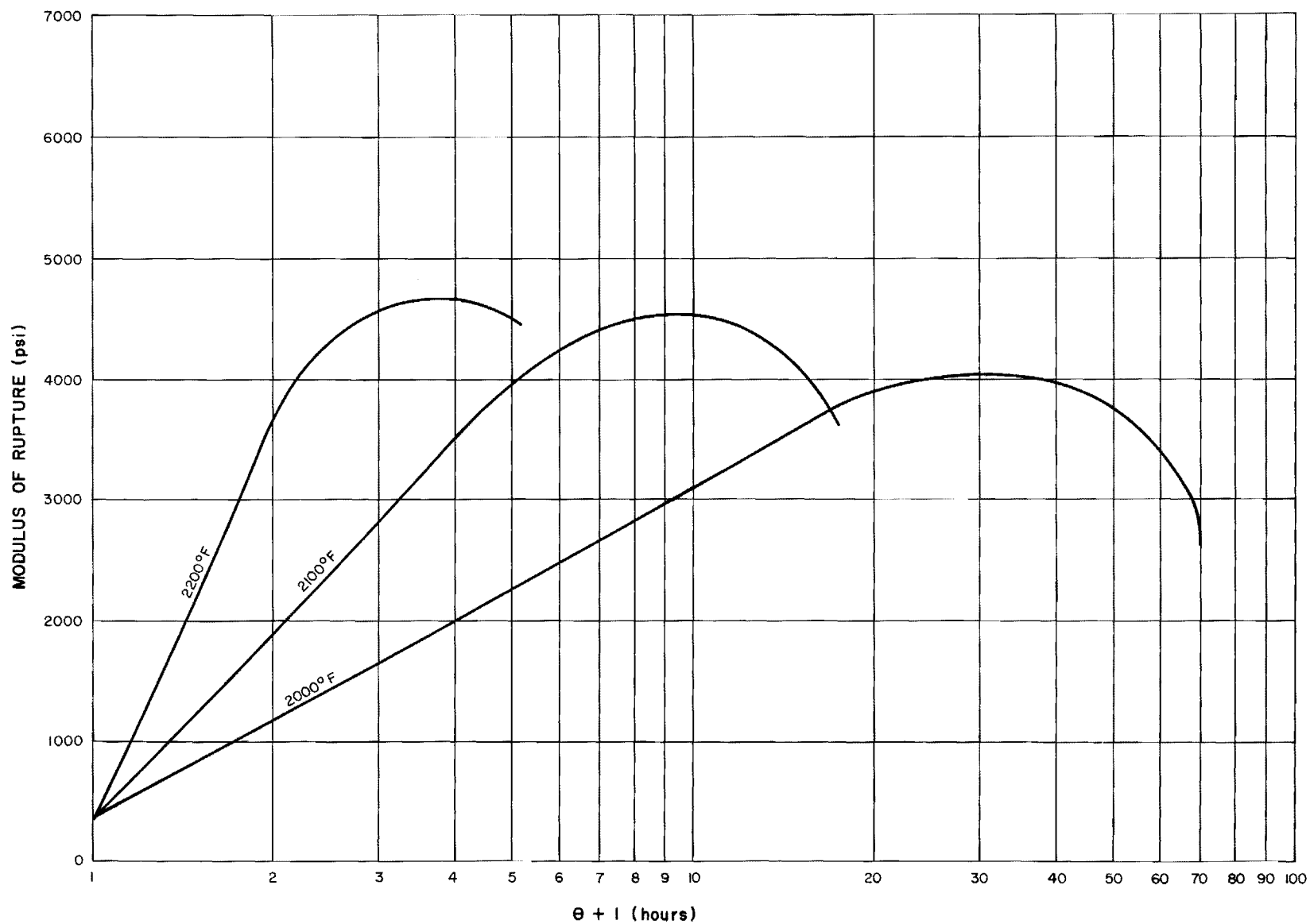


Figure 1. Modulus of Rupture of Slip Cast Fused Silica as a Function of the Firing Time in Steam.



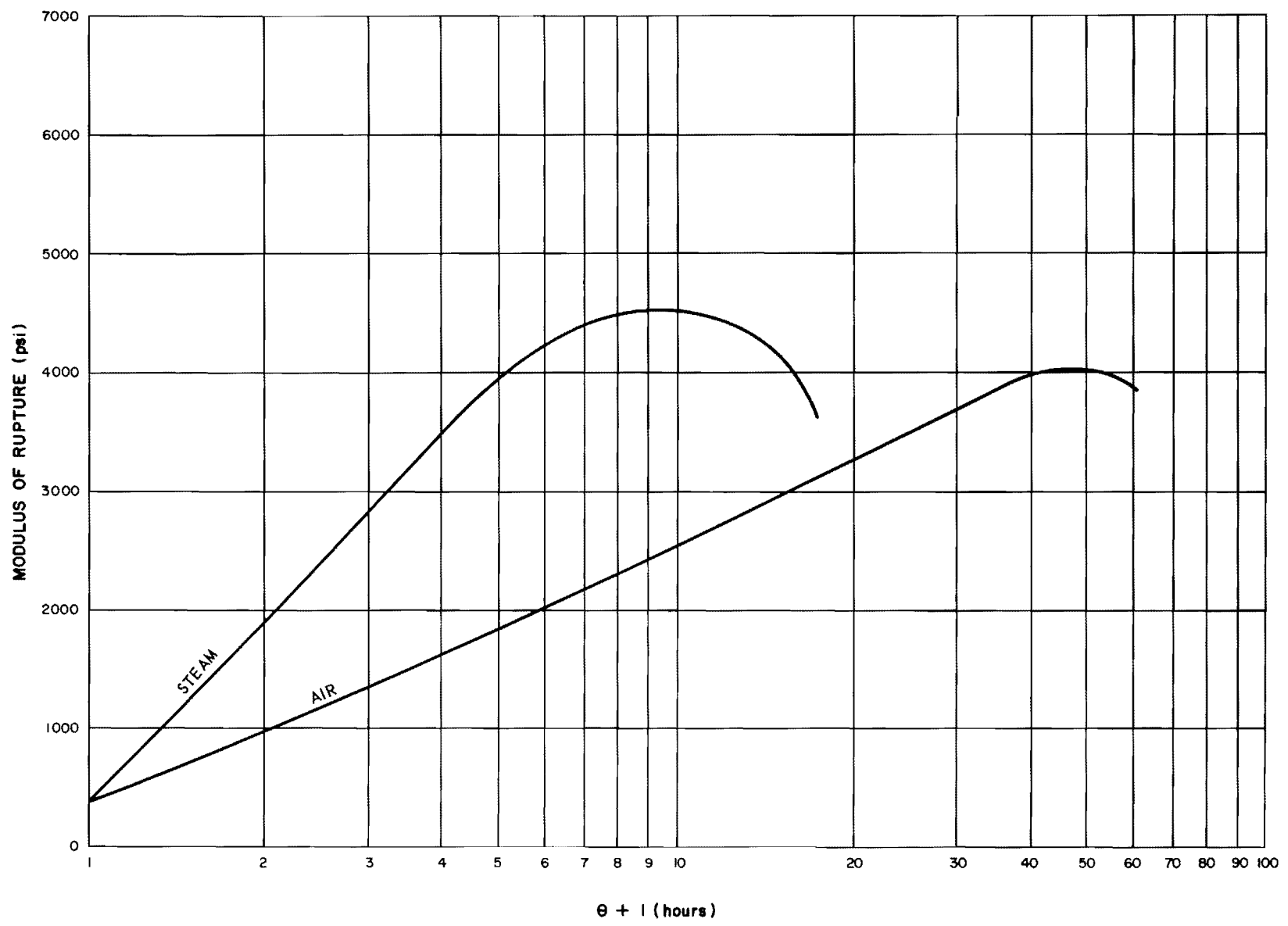


Figure 2. Comparison of 2100° F Strength Profiles for Slip Cast Fused Silica in Steam Firing and Air Firing.

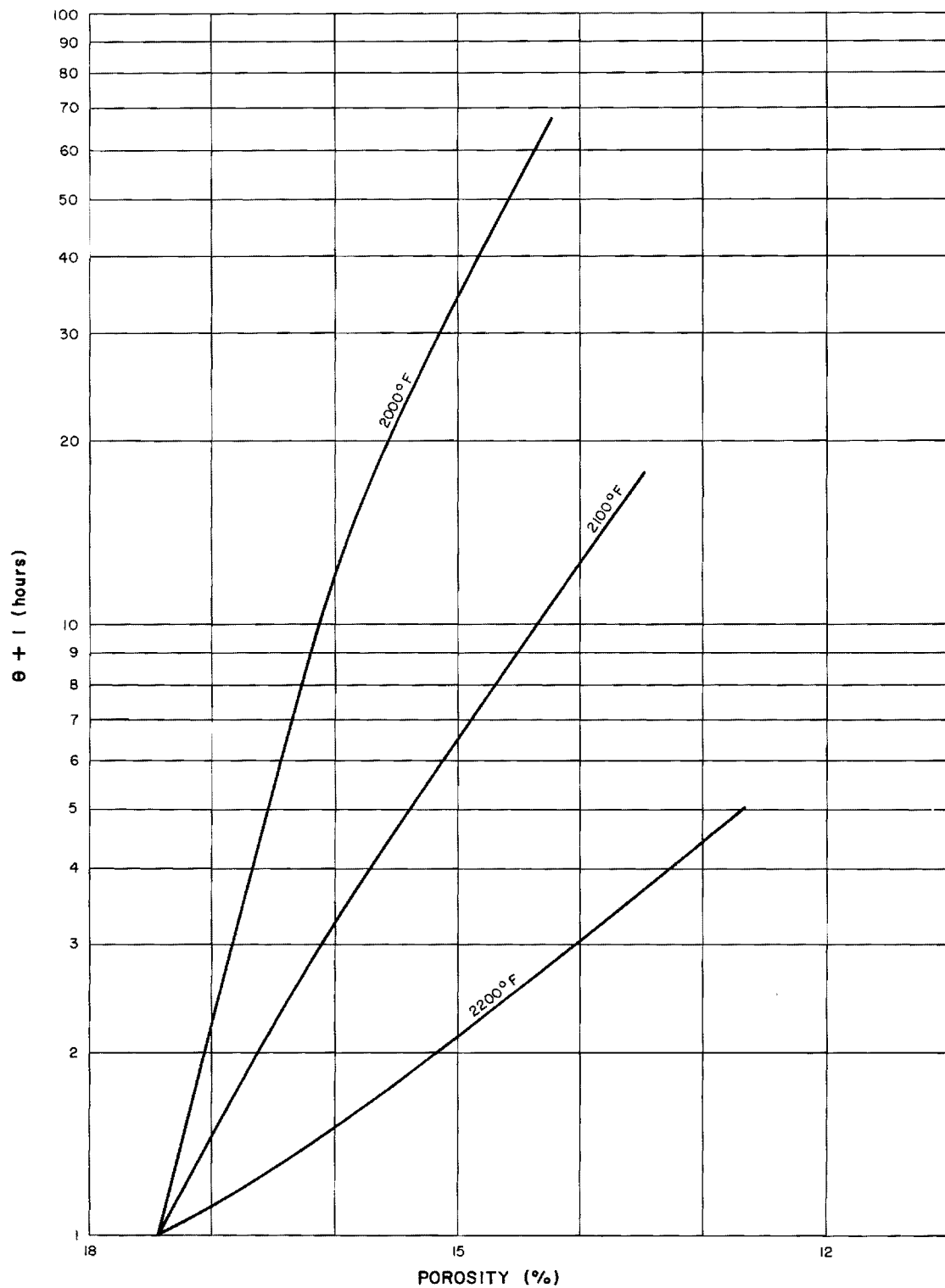


Figure 3. Porosity of Slip Cast Fused Silica as a Function of the Firing Time in Steam.

porosity is attained at approximately the same time as the maximum strength, no such minimum was reached in any of the steam firings. In addition, in the air firings the minimum porosity reached was approximately 14.2 per cent in the temperature range 2000-2200° F. In the steam firings, the porosity reached a low of 12.6 per cent in the longest 2200° F firing and showed no sign of minimizing even then. It is of interest to note that the maximum strengthening in steam and air firing occurred at roughly the same porosity.

The bulk density of steam fired fused silica is shown as a function of firing time in Figure 4. In air firing, the bulk density change varied with the logarithm of firing time while, in steam firing, the variation is seen to be linear. As discussed in Appendix B, this implies that the sintering mechanism in steam firing is viscous flow rather than plastic flow, at least through the point of maximum strengthening.

The bulk density changes in steam firing of slip cast fused silica at a steam flow of 0.72 pounds per hour may be represented by

$$\Delta B = \exp \left( 33.5 - \frac{99300}{T} \right) \theta \quad 1)$$

where  $\Delta B$  is the change in bulk density from the initial value of 1.8535 gm/cc,  $T$  is the absolute sintering temperature (°R) and  $\theta$  is the sintering time (hr.). As discussed in Appendix B,

$$\left. \frac{d(\ln \theta)}{d \left( \frac{1}{T} \right)} \right|_{\Delta B = \text{Const}} = 99300 = \frac{E}{R}$$

which, after dimensional conversion, yields an activation energy of 110 kcal per mole for sintering of slip cast fused silica in steam at a flow rate of 0.72 pounds per hour.

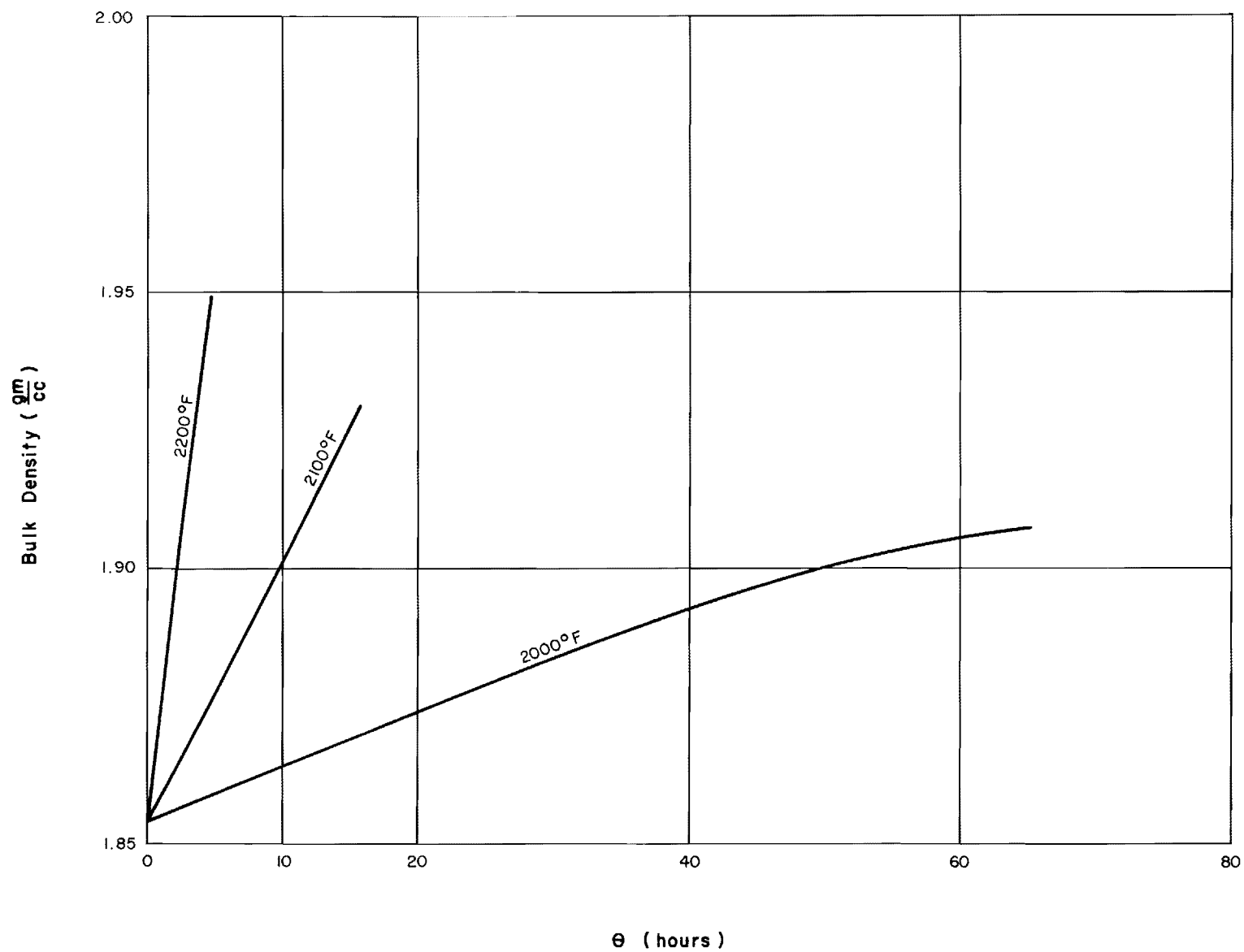


Figure 4. Bulk Density of Slip Cast Fused Silica as a Function of the Firing Time in Steam.

B. Aluminum-Uranium Oxide Reactions

1. Reactions in Al-U<sub>3</sub>O<sub>8</sub> Dispersions of ATR Composition

A 3/8-inch thick plate of Al-U<sub>3</sub>O<sub>8</sub> dispersion, corresponding to the ATR fuel composition, was obtained through the courtesy of the Oak Ridge National Laboratory, Metals and Ceramics Division. The U<sub>3</sub>O<sub>8</sub> used in the dispersion was "dead-burned" Y-12 oxide, probably from the same batch made available by ORNL for the powder metallurgy compacts previously discussed<sup>1</sup>. The composition of the dispersion was 33.79 w/o U<sub>3</sub>O<sub>8</sub>, 66.07 w/o X-800 aluminum, and 0.14 w/o B<sub>4</sub>C. The plate was hot rolled at 500° C to an 8:1 reduction ratio followed by a 15 per cent cross roll.

A reference sample was cut from the as-received plate and half of the plate was vacuum annealed at 500° C for one hour. After the anneal, a second reference sample was cut.

A 3/8- by 3/8- by 3/8-inch sample configuration was selected for convenience. While rectangular geometry is not ideal for differential thermal analysis, the thermal conductivity was felt to be sufficiently high to minimize the resulting inaccuracies from lack of perfectly reproducible sample orientation in the furnace. A hole 1/8-inch in diameter and approximately 3/16-inch deep was drilled in each sample to receive the DTA thermocouple.

a. DTA Tests

Several pellets were subjected to DTA through the apparent reaction temperature range<sup>2</sup>. The resulting DTA curves were not noticeably different from those obtained using pellets of similar composition prepared from Alcoa 140 aluminum and Y-12 oxide by powder metallurgy. A typical DTA chart is shown in Figure 5.

<sup>1</sup>Quarterly Report No. 2, p. 18.

<sup>2</sup>All DTA runs were made at 60° F per minute. The furnace was three times evacuated to approximately 10 microns and backfilled with argon prior to each run. The standard was a similar pellet, previously fired to above 1840° F.

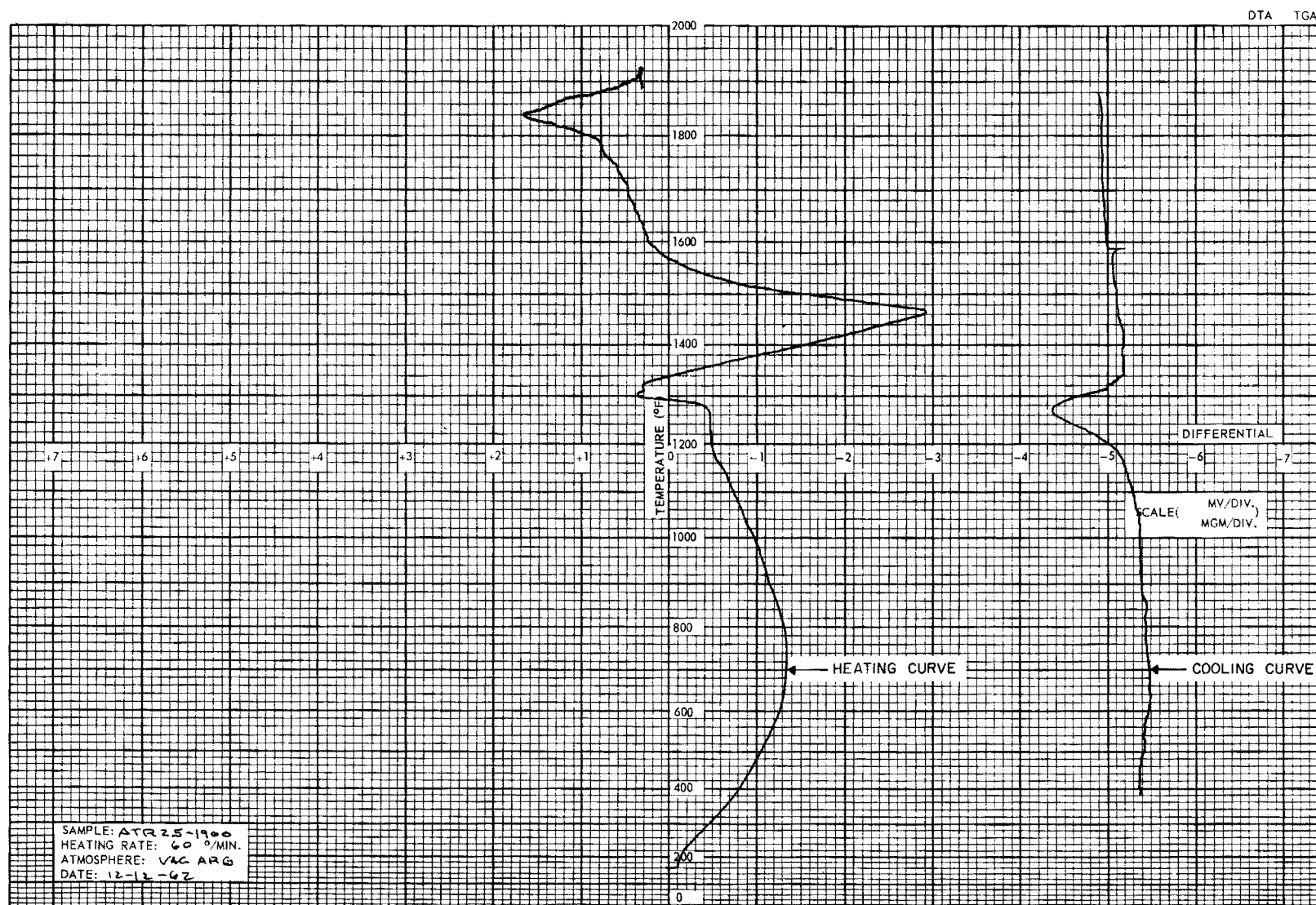


Figure 5. DTA Curve for ATR Plate Specimen.

On heating, an exotherm was invariably noted, peaking at approximately 1300° F. This exotherm was followed by a large endotherm which peaked at 1430 to 1460° F. This endotherm would be expected to be associated with the melting point of the aluminum but is in apparent conflict with the known melting temperature of aluminum. Analysis of this difference is not simple, however. Although a temperature measurement error of approximately 200° F would be the most convenient assumption, rough calculations show that this conclusion is not warranted. Assuming:

- a. Equal heat input to the sample and standard pellets.
- b. Complete prior reaction of all the  $U_3O_8$  in the standard.
- c. No prior reaction in the unknown.
- d. No phase change other than aluminum melting over the endotherm temperature range.

a temperature differential as high as approximately 230° F could arise between the standard and unknown following complete aluminum melting in the standard as a result of the greater free aluminum content of the unknown. In view of this, until further studies can be made, the assumption that the endotherm is due to aluminum melting and that the temperature measurement is accurate does not seem unreasonable.

In all samples, a second exotherm peaked at approximately 1820-1840° F. During this exotherm, the unknown appeared visually to glow slightly brighter than the standard. This cannot be taken as being indicative of the magnitude of the temperature excursion, however, since visual detection of color differences in this temperature range is quite difficult. Attempts will be made in the future to follow the unknown temperature during this exotherm using optical and two color pyrometry.

In several runs, the DTA recorder was used to follow the unprogrammed cooling of the reacted pellet. Since the cooling rate was approximately twice as rapid as the heating rate, quantitative comparisons could not be made of the heating and cooling DTA traces. Qualitatively, however, it is of interest to note that on cooling only a single exotherm was observed in the position appropriate for the aluminum solidification exotherm and that this exotherm appeared substantially smaller than the aluminum endotherm on heating. Occurrence of a cooling exotherm is a reasonable result since the unknown would be expected to contain more free aluminum than the standard, even after the heating cycle. The excess should be somewhat less than during the heating cycle, however, provided a reaction did occur in the unknown. An exotherm would thus be expected on cooling although it should be less prominent than the heating endotherm.

In order to explore the DTA plots further, a series of samples was subjected to heating at 60° F to maximum temperatures of 1000° F to 1900° F in 100° F increments. After the maximum temperature was reached, the sample was allowed to cool in the furnace while DTA recording was continued. The aluminum endotherm on heating was compared qualitatively with the exotherm on cooling. Below 1500° F maximum temperature, no conclusive comparison could be drawn since the heating endotherm had not been completed before cooling was begun. The partially complete endotherm and exotherm did appear quite similar, however. The run to a maximum temperature of 1500° F yielded an aluminum endotherm and exotherm of approximately the same size. In the run to 1600° F, the cooling exotherm was reduced to approximately half the area of the heating endotherm. The 1700° F run showed an exotherm reduced slightly further, perhaps to one third the area of the endotherm. The runs to 1800° F and above showed greatly reduced exotherms ranging from about 10 to 20 per cent of the endotherm area. In one run, no exotherm was noted on cooling.



It is possible that adjustments may be made which will permit the relative endotherm and exotherm areas to be used as an index of the amount of aluminum reacting. This possibility is being explored.

b. X-ray Diffraction

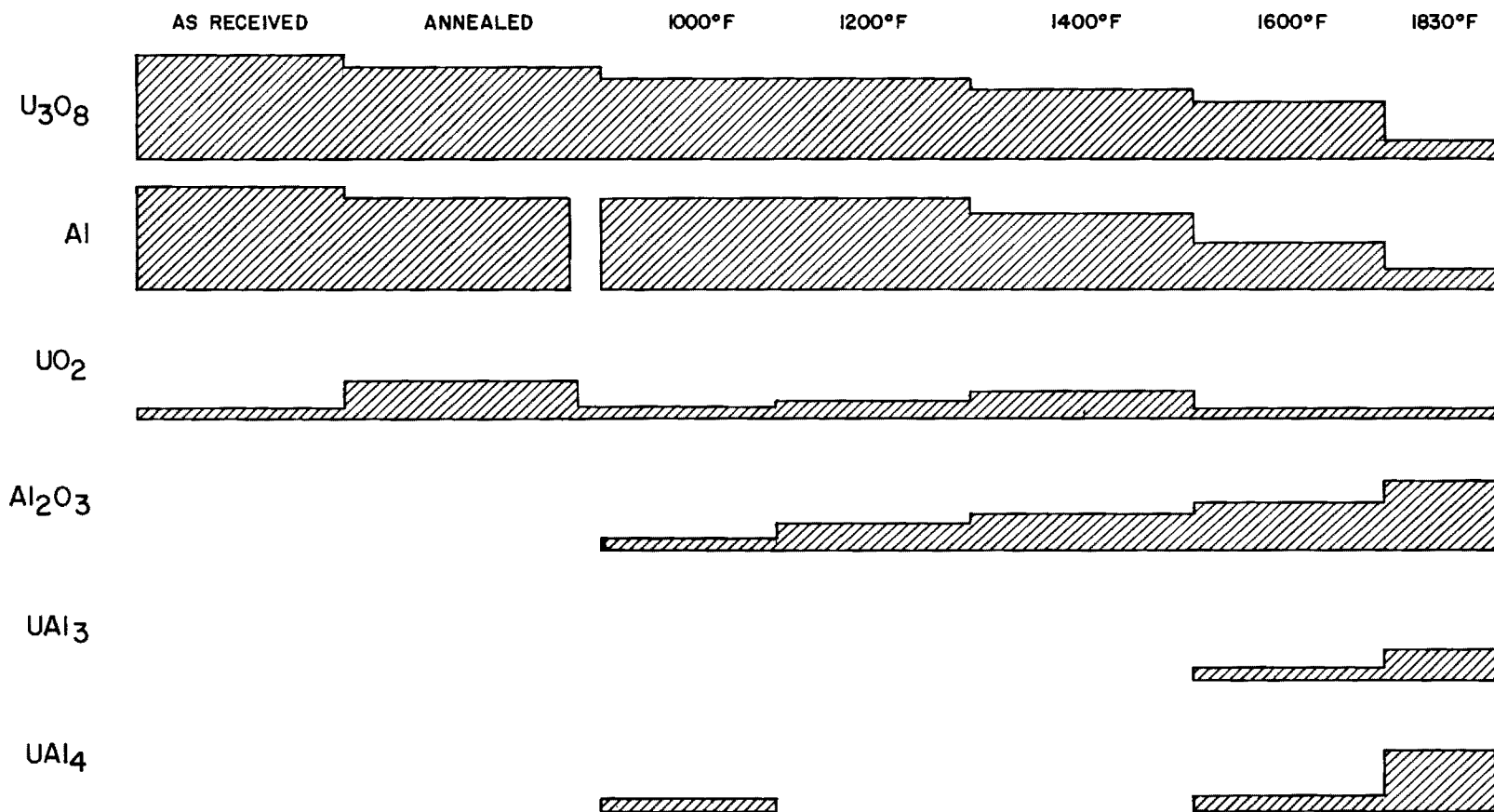
Complete x-ray diffraction traces were made of pellets cut from the as-received plate and from the annealed plate, and of samples heated to maximum temperatures of 1000, 1200, 1400, 1600, and 1830° F. Standards were not available for quantitative comparison but qualitative comparisons of the samples are made in Table II. In addition to the observations listed, low angle strain broadening was noted in the as-received sample but not in any others. No  $\text{UAl}_2$  was detected in any sample.

For convenience, the changes in the various components with increasing maximum temperature during heating are shown in Figure 6. Since this schematic is based on only one sample at each condition and since some variability is noted, this comparison must be taken as being only tentative. Many more samples must be run for confirmation.

The results summarized in Figure 6 agree on some points and disagree on others with previous work at lower temperatures<sup>1</sup>. The low temperature work indicated a two stage reaction with initial reduction to  $\text{UO}_2$  followed by reduction of the  $\text{UO}_2$  to  $\text{UAl}_3$  and  $\text{UAl}_4$  after complete reaction of the  $\text{U}_3\text{O}_8$ . The absence of  $\text{UAl}_3$  and  $\text{UAl}_4$  in the runs up to 1600° F (except for the 1000° F run) with generally increasing  $\text{UO}_2$  indicates that the reduction is two stage over this temperature range. The one disturbing factor is the initial decrease in  $\text{UO}_2$  when the annealed samples were heated. Since the  $\text{U}_3\text{O}_8$  decreased consistently, this would seem to require some U-Al intermetallic formation in all the samples although none was

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<sup>1</sup>Private communication with Mr. C. F. Leitten and Mr. R. C. Waugh, ORNL.



NOTE: No significance should be attached to the absolute height of the bars.  
Intended to show relative changes only.

Figure 6. Phases Identified in Heated ATR Samples.

TABLE II

COMPARISON OF X-RAY DIFFRACTION TRACES FROM HEATED ATR SAMPLES

Condition <sup>1</sup>	$U_3O_8$	Al	$UO_2$	$Al_2O_3$	$UAl_3$	$UAl_4$
As Received (AR)	Strong peaks	Strong peaks	Few poorly defined peaks	No peaks	No peaks	No peaks
Annealed (A)	Peaks slightly smaller than in AR.	Peaks slightly smaller than in AR.	Few well defined peaks, considerably stronger than in AR	No peaks	No peaks	No peaks
1000° F	Peaks smaller than in A.	Definite shift in orientation from AR and A, preventing comparison.	Much smaller than A. Roughly same as AR.	Few well defined peaks	No peaks	Few poorly defined peaks
1200° F	About same as 1000° F.	About same as as 1000° F.	Slightly stronger than 1000° F.	Somewhat stronger than 1000° F.	No peaks	No peaks
1400° F	Slightly smaller than 1200° F.	Much smaller than 1200° F.	Somewhat stronger than 1200° F.	Slightly stronger than 1200° F.	No peaks	No peaks
1600° F	Noticeably smaller than 1400° F.	Noticeably smaller than 1400° F with possible slight orientation shift.	Noticeably smaller than 1200° F.	Stronger than 1400° F.	Few poorly defined peaks	Few poorly defined peaks. Slightly stronger than 1000° F.
1830° F	Much smaller than 1600° F.	Much smaller than 1600° F with probable orientation shift.	About same as 1600° F.	Much stronger than 1600° F.	Several very well defined peaks.	Several very well defined peaks.

<sup>1</sup>Temperatures shown are the maximum reached during heating of the respective test pellets.

seen except in the 1000° F specimen. It is possible, but not likely, that the aluminum orientation shifts in the range 1000 to 1200° F could cause similar effects in the  $\text{UO}_2$  thereby altering the  $\text{UO}_2$  diffraction peaks. Sample to sample variations would seem more likely responsible but, since only one sample was used per point, evaluation of this factor must await further runs.

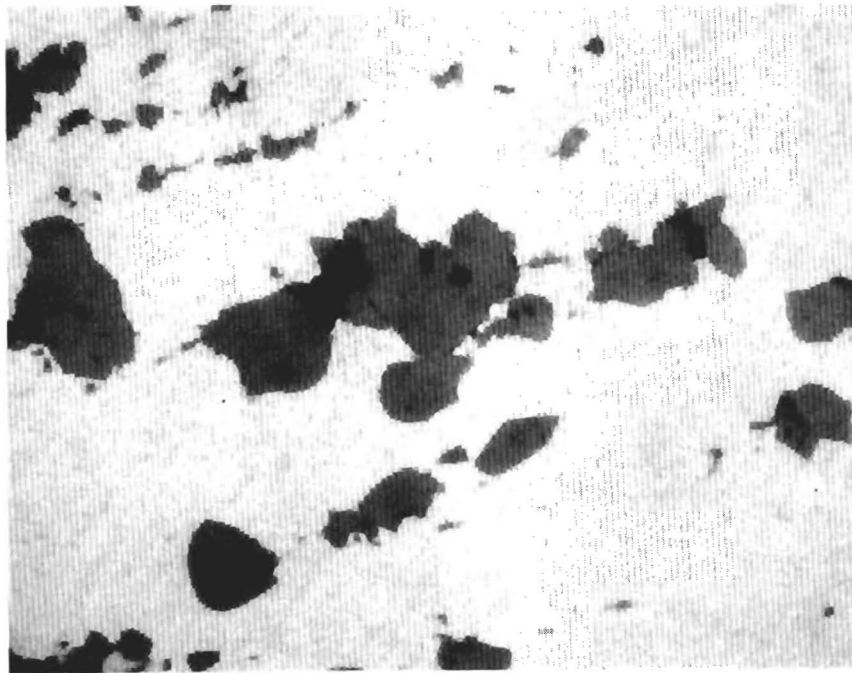
As opposed to the lower temperature work, Figure 6 shows that complete reaction of the  $\text{U}_3\text{O}_8$  prior to  $\text{UAl}_3$  or  $\text{UAl}_4$  formation is not required at higher temperatures. Residual  $\text{U}_3\text{O}_8$  was noted in all the runs in which the U-Al intermetallics appeared.

### c. Metallography

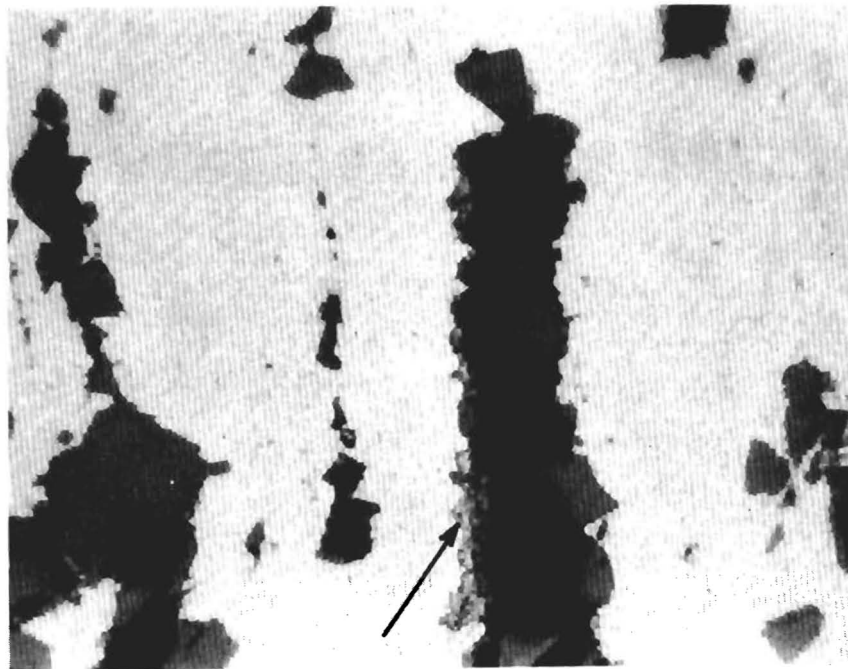
Metallographic examination of the ATR specimens was begun. To date, only six specimens have been studied and these with only one preparation technique. The mechanical polishing method used in preparation of these six specimens showed a pronounced tendency to pull oxide material from the matrix and was far from completely satisfactory. It is hoped that this material loss can be minimized by improvement of the mechanical technique or by application of electropolishing.

In view of the small number of specimens studied and the limited work on preparation technique, any conclusions drawn at this time must be considered tentative and highly speculative. Nevertheless, a brief mention of the metallography appears worthwhile.

Figure 7 shows typical micrographs of the as received material and the sample heated to 1830° F. At least one structure which appears in the 1830° F specimen (see arrow) is absent in the as received material. This structure has the appearance of regions in other samples which were identified as  $\text{Al}_2\text{O}_3$  by electron microprobe analysis. It is of interest to note that this structure appears near many of the particles of presumably unreacted  $\text{U}_3\text{O}_8$ , but is heaviest in the areas



A. AS RECEIVED



B. HEATED TO 1830° F

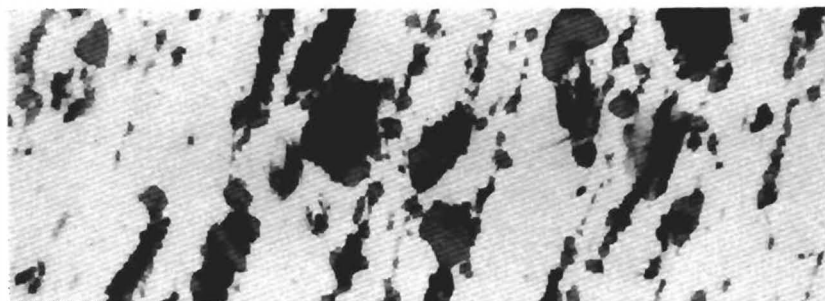
Figure 7. Micrographs of ATR Specimens As-received and Heated to 1830° F. (650X, Unetched).

of most significant material loss during polishing. This would imply that the  $U_3O_8$  reacts to form a phase, probably  $UO_2$ , which is more dense and fragmented hence easier to remove from the matrix during polishing.

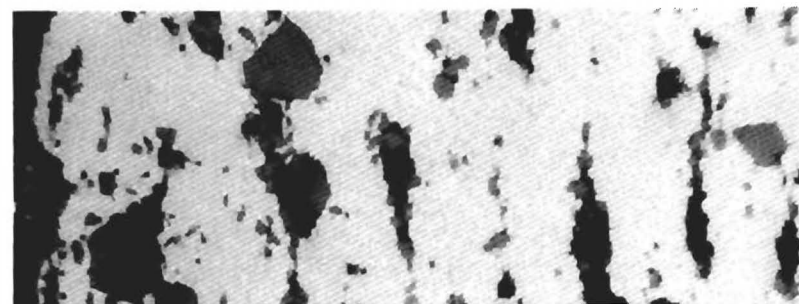
Figure 8 shows micrographs of the as-received material and the specimens heated to 1000, 1200, 1400, 1600, and 1830° F. The zone tentatively identified above as  $Al_2O_3$  appears frequently in the 1830° F specimen, far less frequently in the 1600° F specimen, and only very rarely in the others. In probable conjunction with this, much more material loss is seen in the higher temperature specimens.

The higher temperature specimens also show a fairly heavy concentration of minute pores, indicative of gas evolution. This gas evolution could arise both from dissolved gas in the aluminum and from adsorbed and dissolved gas in the  $U_3O_8$ . The higher temperatures would lead to a greater release of gas from the aluminum through normal solubility changes. In addition, fragmentation of the  $U_3O_8$  should facilitate release of its gases.

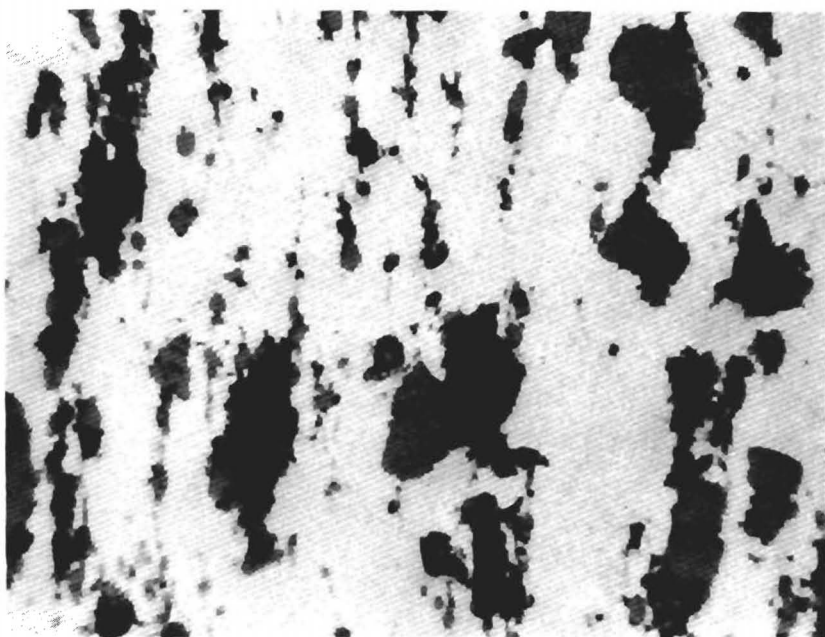
Beginning in the specimens heated to 1200 to 1400° F, the presence of a second phase is noted in the aluminum. In the 1830° F specimen, this second phase is seen to be quite prominent and probably grain boundary precipitation is noted. In view of the much higher concentrations of  $UAl_3$  and  $UAl_4$  indicated by the x-ray analysis of this specimen, the grain boundary precipitate would appear to be  $UAl_4$  and possibly precipitated  $UAl_3$ . In view of the short time available for diffusion of uranium through the liquid aluminum in the lower temperature runs, the uranium concentration should be higher in the vicinity of the reacting  $U_3O_8$ , leading to precipitation of  $UAl_3$  near these particles. In the higher temperature runs, the uranium mobility would be increased and a longer time would be available for diffusion. The improved diffusion would



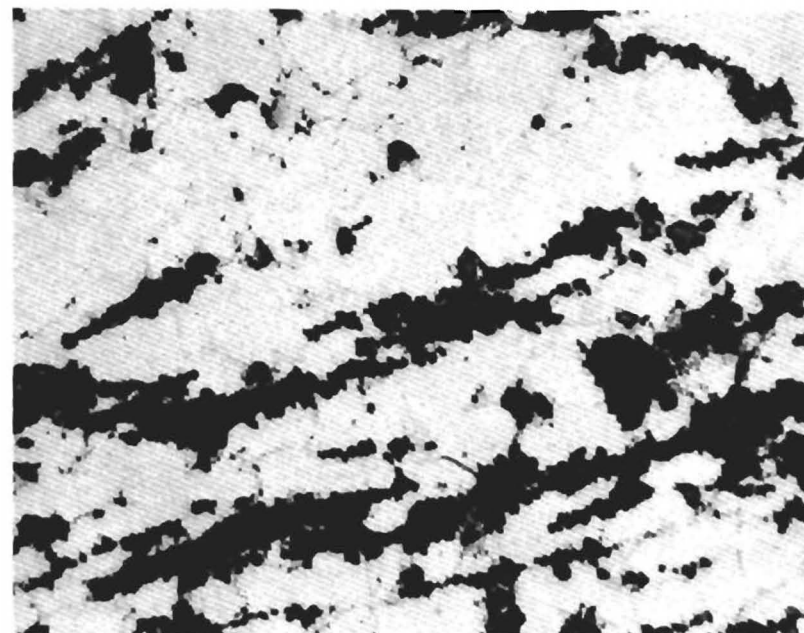
1400° F



AS RECEIVED



1600° F



1830° F

Figure 8. Micrographs of As-received and Heated ATR Specimens.  
(160X, Unetched).

lead to more uniform uranium distribution in the liquid aluminum, hence lower uranium concentrations. At the same time, with increased reaction of  $U_3O_8$ , the total amount of uranium in the liquid phase should increase. The combination of the more uniform distribution, the greater amount of dissolved uranium, and the lower uranium concentrations would promote more prominent and more well dispersed<sup>1</sup> precipitation of  $UAl_4$  or the  $UAl_4$ - $\eta$  solid solution eutectic on cooling through the  $UAl_4$  peritectic temperature ( $1345^\circ F$ ) and the eutectic temperature ( $1184^\circ F$ ). Etching studies were begun to delineate the micro-structure of the metallic matrix.

## 2. Comparison of Al- $UO_2$ and Al- $U_3O_8$ Compacts

Studies were begun to compare reaction tendencies in Al- $UO_2$  and Al- $U_3O_8$  powder metallurgy compacts. Compacts containing 35 w/o  $UO_2$  and 35 w/o  $U_3O_8$  were produced in the usual manner<sup>2</sup>. The starting materials were Alcoa 140 atomized aluminum, hydrothermal  $UO_2$ , and "dead-burned"  $U_3O_8$ <sup>3</sup>. The pellets were subjected to differential thermal analysis in argon at a heating rate of  $60^\circ F$  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 III.

From the preliminary results, it appears that Al- $U_3O_8$  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

---

<sup>1</sup>With respect to the  $U_3O_8$  particles.

<sup>2</sup>Summary Report No. 1, p. 38.

<sup>3</sup>Uranium oxides furnished through the courtesy of the Metals and Ceramics Division, Oak Ridge National Laboratory.



in Al-UO<sub>2</sub> 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 are now being run to permit statistical evaluation.

TABLE III  
DTA DATA FOR Al-UO<sub>2</sub> AND Al-U<sub>3</sub>O<sub>8</sub> COMPACTS

<u>System</u>	<u>Temperature of Exotherm Peak</u> (°F)	<u>Peak Height</u> (mv)	<u>Peak Area</u> (in <sup>2</sup> )
Al-35 w/o UO <sub>2</sub>	1820	1.9	0.61
Al-35 w/o U <sub>3</sub> O <sub>8</sub>	1780	1.2	0.52

#### IV. DISCUSSION

As in previous studies, the evaluation of the effects of equilibration time in the ring test showed a significant firing to firing variation which masked any possible soaking time effects. This observation continues to support the decision to limit the number of testing temperatures studied and to use sufficient samples for statistical correlation at each point.

The modified water supply system for the steam firing furnace proved highly satisfactory in improving the reproducibility of firing. The results of the steam firing study continued to be most intriguing, offering the possibility of much more efficient firing. In view of the strengthening kinetics observed, steam appears to decrease the yield strength and viscosity while producing structural or chemical changes which increase the activation energy. Since the steam will not necessarily affect the devitrification and sintering kinetics in the same manner, different steam flow rates may change the relative rates of sintering and devitrification and have a significant effect on both the strengthening kinetics and maximum strength attainable in quench-firing.

The results of the steam firings to date indicate that further investigations are highly desirable. A better understanding of the effects of water vapor is essential from the standpoint of both more efficient fabrication and service evaluation in water-vapor-bearing environments. If such a program cannot be completed during the current year, continuation past completion of the remaining work with silica is strongly recommended.

The results of the first studies of the  $\text{Al-U}_3\text{O}_8$  dispersion of ATR composition are both informative and consistent with past work with pressed compacts. The early appearance of  $\text{UO}_2$  prior to formation of  $\text{UAl}_3$  and  $\text{UAl}_4$  offers support for

the suggestion of a two stage reaction. The observation of residual  $U_3O_8$  in all the specimens indicates that complete reduction to  $UO_2$  does not necessarily precede formation of  $UAl_3$  and  $UAl_4$ .

The behavior of the  $UO_2$  in the annealed and heated specimens is rather strange. If the one annealed specimen analyzed is truly representative of all the starting material, reduction of some  $UO_2$  must have occurred upon heating of the annealed specimens. This conclusion follows from the decrease of both  $UO_2$  and  $U_3O_8$  noted upon heating the annealed specimens. If the  $UO_2$  were reduced, some U-Al intermetallics should have been found in all the specimens, not just in the 1000, 1600, and 1830° F pellets. A further disturbing, possibly related, fact is that the metallographic examination did not yield results which could be correlated directly with the x-ray results. A new phase was apparent in the metallic matrix in all specimens heated to or above 1400° F but, with the exception of the 1000° F specimen, no new x-ray peaks were noted in specimens heated to less than 1600° F. These two facts could be reconciled if the x-ray detection efficiency for the U-Al intermetallics were fairly low. More runs are obviously necessary before this point can be resolved.

The initial tests of Al- $UO_2$  specimens showed behavior similar to that of Al- $U_3O_8$ . Since so few specimens have been run, it is difficult to state the significance of the apparently higher temperature, compared with Al- $U_3O_8$ , required for reaction and the apparently more energetic reaction. This behavior is at least not inconsistent with that to be expected from  $UO_2$  from two different sources. If a two stage reaction is operative in Al- $U_3O_8$ , and if the high temperature exotherm is caused by secondary reduction of the  $UO_2$  produced in the first stage, the high temperature reactions in Al- $U_3O_8$  and Al- $UO_2$  should be mechanistically similar. Since the  $UO_2$  in the two cases does not arise from

Quarterly Report No. 3, Project No. B-153

the same source, however, and is not even necessarily of the same stoichiometry, differences in the energetics should not be surprising. More clarification should be possible with the additional samples now being run.

Quarterly Report No. 3, Project No. B-153

V. PERSONNEL

The work discussed in this report was conducted in the High Temperature Materials Branch, Mr. J. D. Walton, Head. This 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. S. H. Bomar	Group Leader
Mr. A. R. Colcord	Group Leader
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Mr. P. A. Darius	Technician
Mr. A. C. Evans	Technician
Mr. W. M. Linstrom	Technician
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High Temperature Materials Branch

*F. Bellinger*  
F. Bellinger, Chief  
Chemical Sciences and Materials Division

VI. APPENDICES

APPENDIX A

Data From Study of Ring Test Re-Heat Time

Firing Data

<u>Firing</u>	<u>Heat-up-time (min.)</u>	<u>Minimum Temp. (°F)</u>
1st	34	1960
2nd	29	2000
3rd	29	2020

Tensile Strength Data\*

	<u>No Warm-up</u>	<u>Warm-up to Preheat Temp.</u>	<u>Warm Five Min. After Preheat Temp.</u>	<u>Avg. Over Firings</u>
1st Firing	1180 } 898 } 1049** 1108 } 1010 }	1036 } 1090 } 1089 1181 } 1048 }	1000 } 1362 } 1116 1093 } 1008 }	1085
2nd Firing	970 } 890 } 850 760 } 780 }	1071 } 768 } 889 830 } 888 }	1265 } 1191 } 1126 870 } 1179 }	955
3rd Firing	793 } 790 } 834 900 } 854 }	910 } 1055 } 1005 803 } 1250 }	855 } 838 } 874 895 } 908 }	904
Avg. over warm-ups	911	994	1039	

\* Since the tensile strength factor was expected to be the same for each ring (the dimensions did not vary significantly from ring to ring), the load required to rupture each ring was displayed. This was justified because of interest only in the differences between testing methods.

\*\* Figures shown by braces are averages for the samples enclosed by the braces.

APPENDIX B

Sintering in Steam Firing

Application of the viscous flow model<sup>1</sup> to the sintering of slip cast fused silica indicated that

$$\left. \frac{d(\ln \theta)}{d\left(\frac{1}{T}\right)} \right|_{\Delta B = \text{Const}} = \text{constant} = \frac{E}{R} \quad \text{B-1)}$$

where  $\theta$  represents the sintering time,  $T$  is the absolute sintering temperature,  $E$  is the activation energy, and  $R$  is the gas constant. Since this condition was met in the steam firing of the silica, the prevailing sintering mechanism would appear to be viscous flow.

Examining this case more closely, if the argument<sup>2</sup> for relating the bulk density change to the sintering lens volume is accepted, it is evident that this condition may be applied to any functional equation desired. Consequently, Equation 11<sup>3</sup> may be modified to yield

$$\frac{d(\Delta B)}{d\theta} \doteq A_2 e^{-\frac{E}{RT}} [F_1(\Delta B) - S'F_2(\Delta B)] \quad \text{B-2)}$$

where  $A_2$  is a constant.

---

<sup>1</sup>Quarterly Report No. 2, p. 26.

<sup>2</sup>Quarterly Report No. 2, p. 30.

<sup>3</sup>Quarterly Report No. 2, p. 29. Equations 10 and 11 contain typographical errors. They should read

$$\eta_{\infty} = A_0 e^{\frac{E}{RT}} \quad 10)$$

$$\frac{dV_l}{d\theta} \doteq A e^{-\frac{E}{RT}} [F_5(V_l) - S'F_6(V_l)] \quad 11)$$



At a given temperature, if the sintering bulk density change is linear with time

$$F_1 (\Delta B) - S' F_2 (\Delta B) = \text{constant} \quad \text{B-3)}$$

Since  $\Delta B$  is not single valued, this can be true only if the functions  $F_1$  and  $F_2$  are constant or compensating, i.e. of the same form. In either case, if the yield stress is significant and varies significantly with temperatures, the variation in densification curve slope with  $\frac{1}{T}$  would be other than exponential.

The logarithms of the slopes of the densification curves are plotted as a function of  $\frac{1}{T}$  in Figure 9. Since the variation is exponential, three possibilities are evident:

- a.  $S' = 0$ .
- b.  $S'$  is significant
- c.  $S'$  is negligibly dependent on temperature.

Case c would not seem physically reasonable. Either case a or case b would be possible and would constitute a proper basis for identifying the sintering mechanism in steam firing of fused silica as viscous flow. Further work is obviously necessary to support this conclusion.

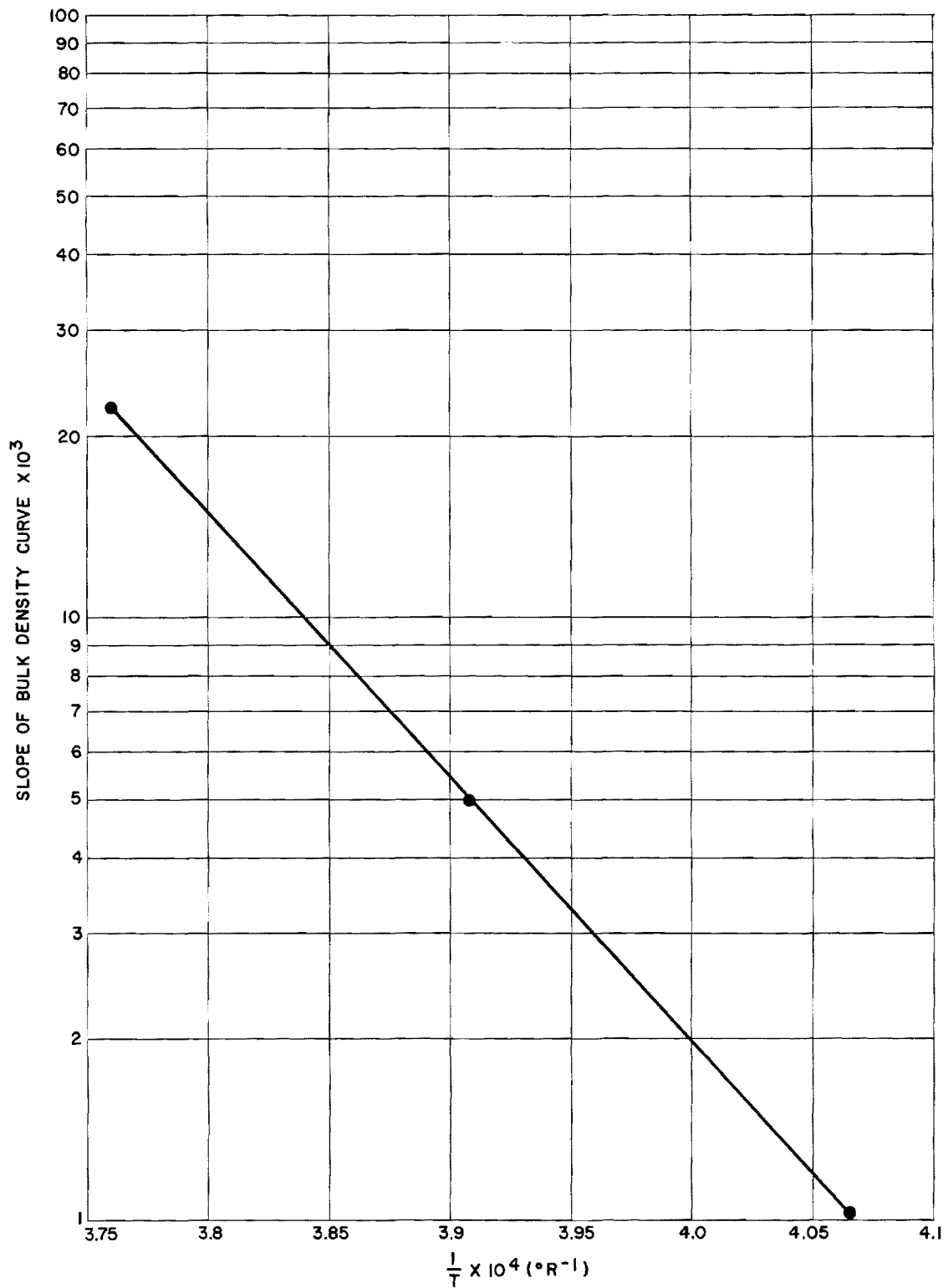


Figure 9. Arrhenius Plot for Bulk Density in Steam Fired Slip Cast Fused Silica.

VII. PRIOR REPORTS

Previous reports issued under this contract are:

1. Monthly Letter Reports Nos. 1 - 49, Issued each month since December 1958.
2. Progress Report No. 1, August 1959. Issued as ORO-209 by OTS, Department of Commerce.
3. Progress Report No. 2, Part 1, August 1960, Issued as ORO-325 by OTS, Department of Commerce.
4. Progress Report No. 2, Part 2 (Declassified), August 1960.
5. Progress Report No. 3, August 1961.
6. Quarterly Report No. 1, April 1962.
7. Summary Report No. 1, July 1962.
8. Quarterly Report No. 2, October 1962.

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QUARTERLY REPORT NO. 4

PROJECT NO. B-153

MATERIALS FOR HIGH TEMPERATURE  
NUCLEAR ENGINEERING APPLICATIONS

By J. D. Fleming, J. W. Johnson,  
Paul Boland, and S. H. Bomar

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

1 April



Engineering Experiment Station  
**GEORGIA INSTITUTE OF TECHNOLOGY**  
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ENGINEERING EXPERIMENT STATION  
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Atlanta, Georgia

QUARTERLY REPORT NO. 4

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Oak Ridge Operations Office  
Oak Ridge, Tennessee

January 1, 1963 to April 1, 1963



Quarterly Report No. 4, Project No. B-153

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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.

This report covers the period from January 1, 1963 to April 1, 1963.

## 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  $U_3O_8$ . Since Al- $U_3O_8$  dispersions are in common use as reactor fuels, the results of this study are obviously of interest in hazards evaluation. Several special studies of Al- $U_3O_8$  dispersions are included in the program to assist hazards evaluation.

## II. SUMMARY

A treatment of the early cristobalite growth process in the firing of slip cast fused silica predicted a cubic time variation in cristobalite. Analyses by x-ray diffraction yielded growth curves in agreement with this prediction. Based on these results, the initial cristobalite content of the fused silica slip is approximately 0.5 per cent.

Consideration of the conditions for maximum strengthening in fired slip cast fused silica led to a functional analysis of the effects of firing temperature on the time required for maximum strengthening. The activation energy for this strengthening process, indicated by the analysis, is 205 kcal per mole.

The study of sintering in slip cast fused silica under one atmosphere of steam was completed. Application of the prediction of cubic time variation of cristobalite content to the steam fired bars indicated an initial cristobalite content in the slip of 0.5 per cent, in excellent agreement with the air data. The one atmosphere steam data were also used to determine the activation energy for devitrification in one atmosphere steam. This activation energy is approximately 98 kcal per mole.

Investigations were begun of firing slip cast fused silica under two atmospheres of steam. The preliminary results of this study indicate sintering even more rapid than in one atmosphere steam. The maximum moduli of rupture and firing time for maximum strength at 2100° F are approximately 4200 psi and 48 hours in one atmosphere air, 4600 psi and 9.5 hours in one atmosphere steam, and 6100 psi and 5 hours<sup>1</sup> in two atmosphere steam.

---

1. Preliminary data

Investigations were made of the influence of application of pressure and vibration during slip casting of fused silica. These studies showed that application of 60 psig lowered the casting time of 3/4-in. diameter bars from 150 to 17 minutes at the cost of a decrease in cast bulk density from 1.854 to 1.846 gm per cc. A 60 cps axial vibration of 0.015-in. amplitude increased the cast bulk density in 60 psig cast bars to 1.849 gm per cc. without producing a noticeable increase in casting time.

Modification and testing of the high temperature x-ray diffraction system were begun. The modification was almost completed and measurement of reaction rates in ATR compacts should begin early during the next quarter.

Investigations were begun to determine the feasibility of measuring the aluminum conversion and reaction energy by differential thermal analysis (DTA) of reacting Al-U<sub>3</sub>O<sub>8</sub> 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-U<sub>3</sub>O<sub>8</sub> composites appears promising although only two samples have been run.

III. EXPERIMENTAL WORK

A. Slip Cast Fused Silica

1. Effects of Air Firing

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<sup>1</sup> indicated that the initial growth stages should produce a cubic time variation in the cristobalite content. The preliminary cristobalite analyses are shown as a function of firing time according to the criterion in Figure 1.

While the cristobalite data are drawn from too few samples for satisfactory statistical reliability, it is of interest to note the reasonable agreement between the expected and observed initial cristobalite growth. Assuming that this picture is correct, Figure 1 indicates that the fused silica slip is not initially free of cristobalite. For the slip used in this study, an original cristobalite content of the order of 0.5 per cent appears likely. Further cristobalite analyses now under way should provide a more valid test for this early devitrification hypothesis.

The strengthening process during firing of slip cast fused silica is probably, as has been suggested previously, regulated by two competing mechanisms, sintering due to bulk flow and bond disruption following devitrification. These processes are illustrated schematically in Figure 2. The increased bonding resulting from plastic flow of the silica<sup>2</sup> should cause a continuous strengthening. The devitrification occurring during firing should produce cristobalite "inclusions" in the bonding junctures between particles. Since the silica is air quenched following firing, these cristobalite inclusions

---

1. Appendix A.

2. Quarterly Report No. 2, p. 11-13.

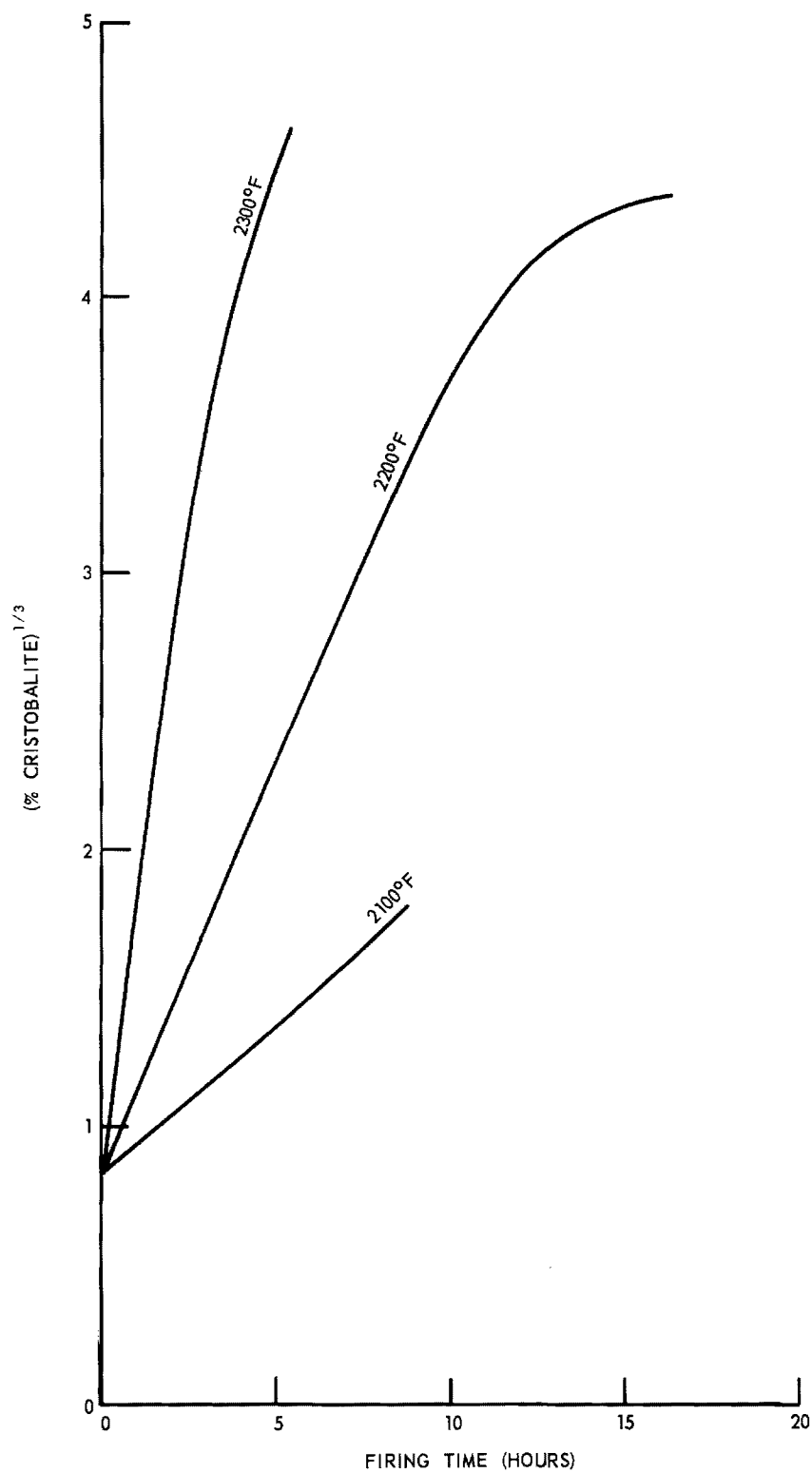


Figure 1. Cristobalite Content of Slip Cast Fused Silica as a Function of Firing Conditions. (Preliminary Results)



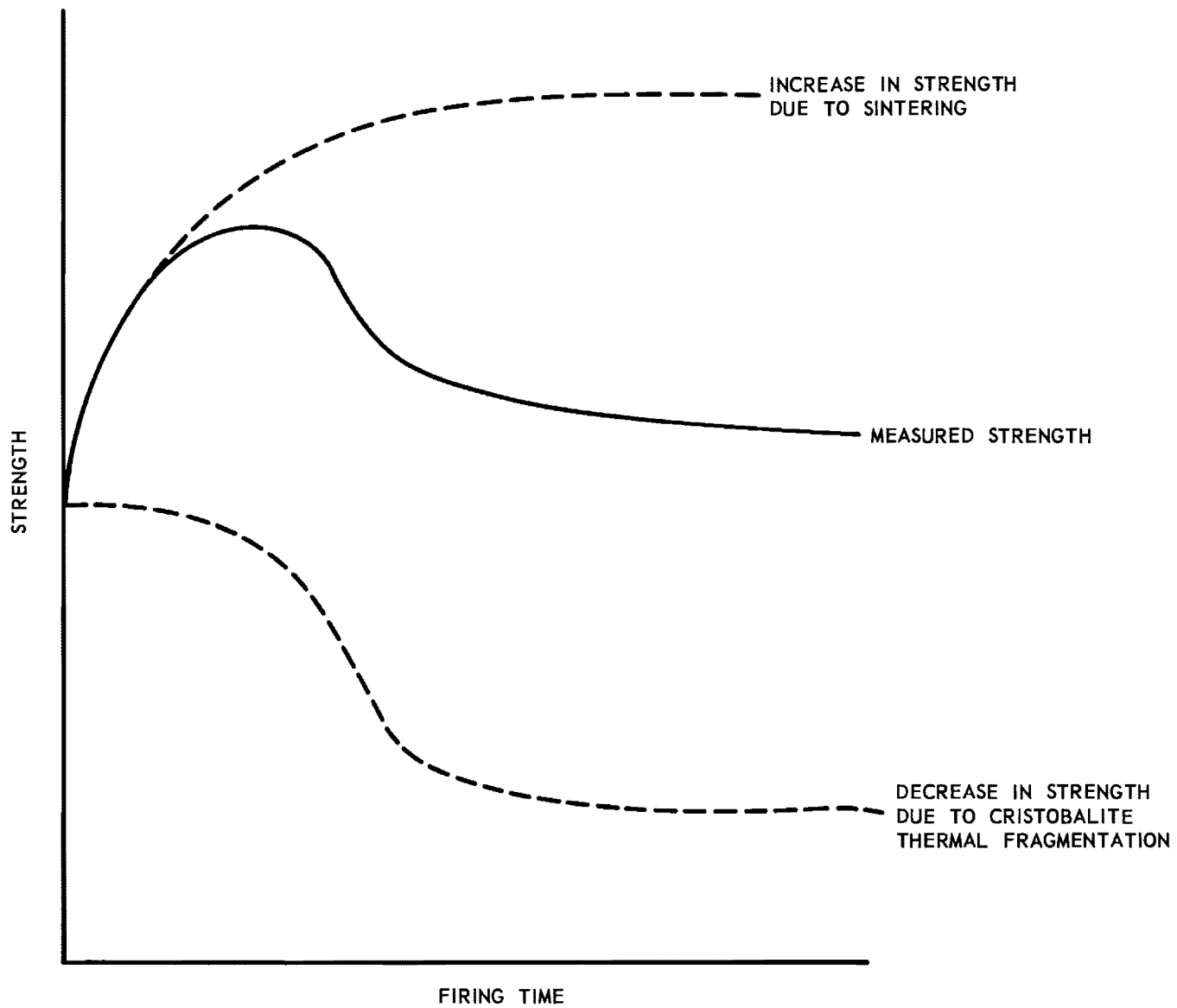


Figure 2. Hypothetical Strengthening Processes in Slip Cast Fused Silica.

will be subjected to thermal stressing upon cooling and, above a critical size, will fracture, resulting in bond rupture. The extent of this bond rupture should increase with increasing cristobalite content and inclusion size. The fired strength of the fused silica would then be the algebraic summation of the strengthening and weakening effects of these two processes, as shown in Figure 2.

The preliminary x-ray cristobalite analyses indicate that the peak strength in air firing is reached at a roughly constant cristobalite content of approximately five per cent regardless of the firing temperature. This is not an unexpected result. Once the cristobalite inclusions reach the size productive of thermal cracking, fragmentation of the cristobalite should be essentially complete as a result of rapid crack propagation characteristic of ceramics. In combination with the strong dependence on time of the extent of cristobalite formation<sup>1</sup>, this would imply that the disruption due to cristobalite fracture should be capable of over-riding the slower sintering strengthening at almost any level of firing. In addition, the notch sensitivity typical of ceramics would magnify the effects on strength of any cracks resulting from cristobalite fracture. This reasoning led to an analysis for devitrification<sup>2</sup> based on observation of the time required for maximum strengthening as a function of firing temperature. This analysis, quite similar to the previous sintering analyses<sup>3</sup> indicated that

$$\frac{d(\ln \theta_i)}{d(\frac{1}{T})} = \text{constant} = \frac{E}{R} \quad 1)$$

- 
1. Appendix A
  2. Appendix B
  3. Quarterly Report No. 2, p. 26-31.  
Quarterly Report No. 3, p. 33-34.

where  $\theta_1$  is the time to reach maximum strength, T is the absolute firing temperature, R is the gas constant, and E is the activation energy for the cristobalite formation process. The times for maximum strengthening<sup>1</sup> are plotted according to Equation 1 in Figure 3. The activation energy indicated by Figure 3 is 205 kcal per mole. Since the process characterized by this activation energy is probably quite complex, some caution is necessary in referring to the energy as the activation energy for devitrification. Although this may prove to be the case, direct determination of the devitrification activation energy from x-ray analysis for cristobalite appears essential for confirmation. In addition, the other devitrification-dependent parameters should be given a similar treatment for comparison.

The modulus of rupture data were extended to complete definition of the strengthening contour for slip cast fused silica. This contour is shown in Figure 4.

## 2. Effects of Steam Firing

### a. One Atmosphere Steam:

Slip cast fused silica bars fired under one atmosphere absolute of steam<sup>2</sup> were regrouped into the sets in which they were fired. Each group was crushed to -200 mesh and a sample was drawn for cristobalite analysis by x-ray diffraction. Since the early devitrification process would be expected to be similar in air and in steam, the same analysis was applied to the steam and air firings<sup>3</sup>. Figure 5 shows the one atmosphere steam firing cristobalite data plotted as indicated by the analysis of Appendix A. It is of interest to

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1. Quarterly Report No. 1, p. 22.
  2. Quarterly Report No. 3, p. 7-13.
  3. Appendix A.

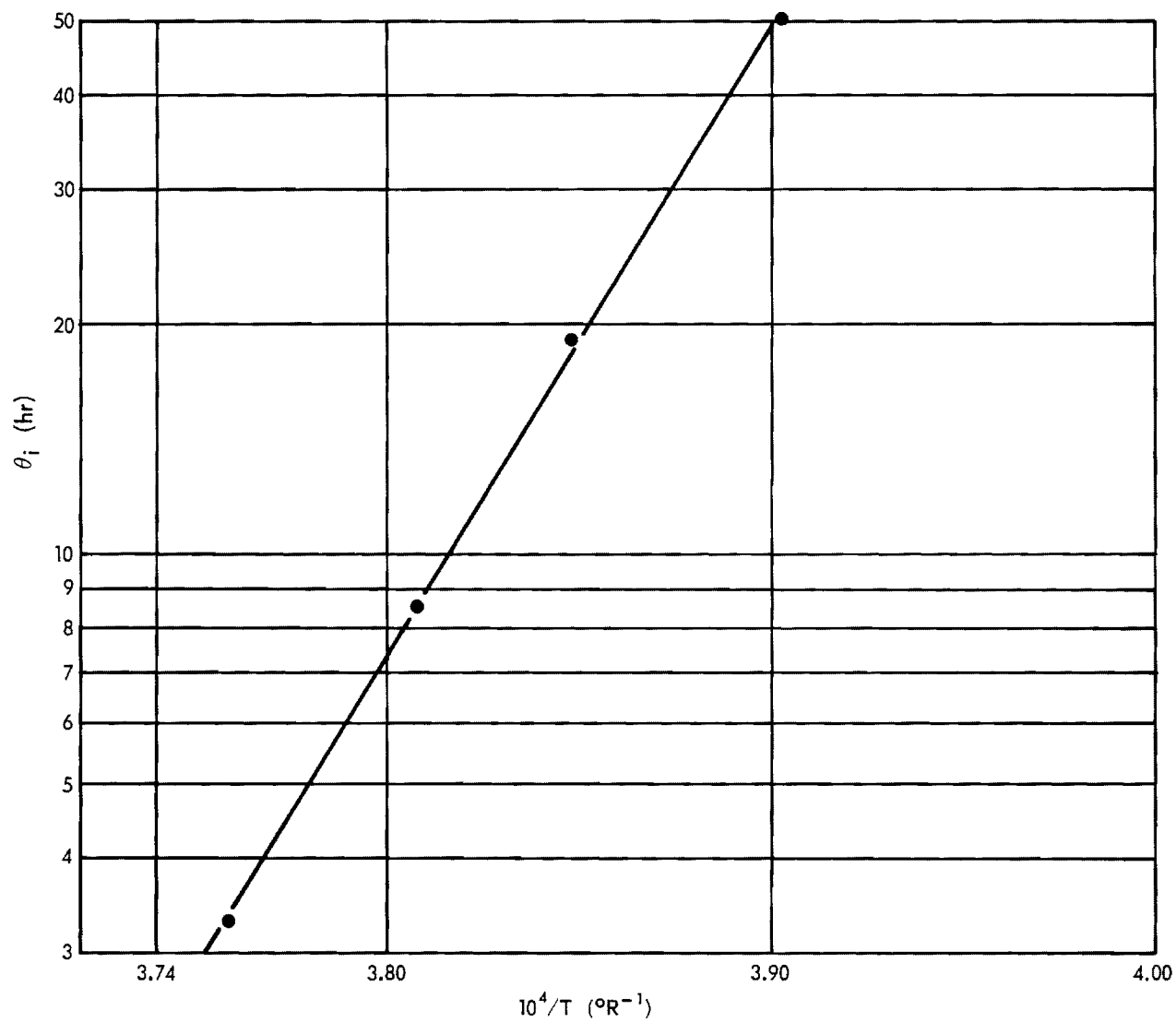


Figure 3. Time to Reach Maximum Strength in Slip Cast Fused Silica During One Atmosphere Air Firing Vs. Reciprocal of Absolute Sintering Temperature.

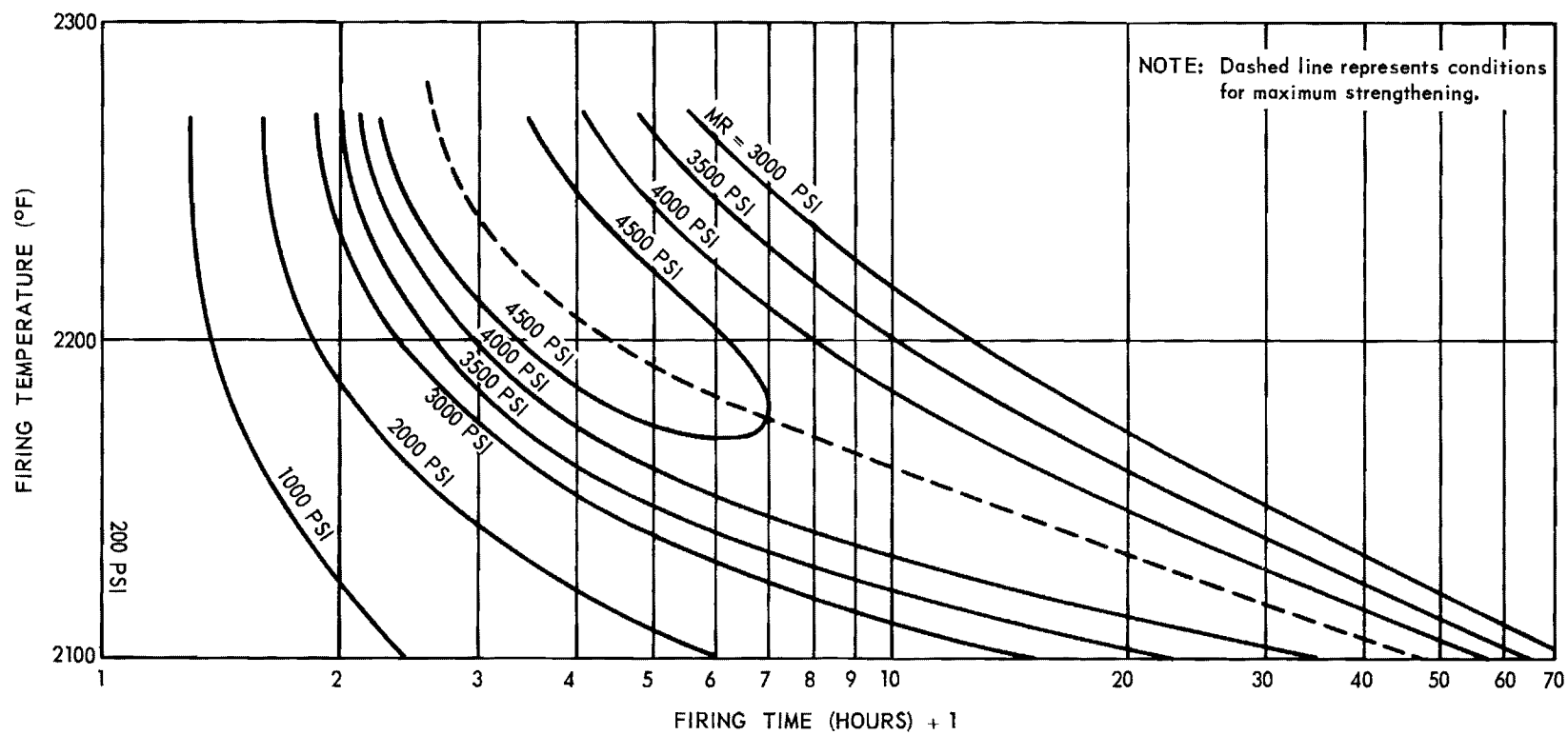


Figure 4. Modulus of Rupture Contour for Slip Cast Fused Silica Fired Under One Atmosphere of Air.

note that the steam and air firing data indicate approximately the same initial cristobalite content, approximately 0.5 per cent, in the slip.

While insufficient data were available for a determination of the activation energy in air devitrification, the steam data were reliable enough to permit this analysis. The Arrhenius plot for devitrification of slip cast fused silica under one atmosphere of steam is shown in Figure 6. From the slope of this curve, an activation energy of 98 kcal per mole was calculated.

The firings in one atmosphere steam were extended to permit determination of the strength contour. This contour is shown in Figure 7.

b. Two Atmosphere Steam:

A total of 308 fused silica bars, 3/4-in. in diameter by 5-5/8-in. long, was cast in one piece molds using the graphite mold release. The bars were fired in sets of 11 using a small tube furnace. Firings were made at 2000°F for 4, 8, 16 and 24 hours, at 2100° F for 1, 2, 4, 6, and 8 hours, and at 2200° F for 1/2, 1, 2 and 4 hours. Triplicate firings were made at 2100° F for 6 and 8 hours, and duplicate firings were made at all other conditions. In all cases, 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 a vacuum was drawn on the heating tube.
- d) The tube was backfilled with argon, and a vacuum was drawn. This step was repeated four times.

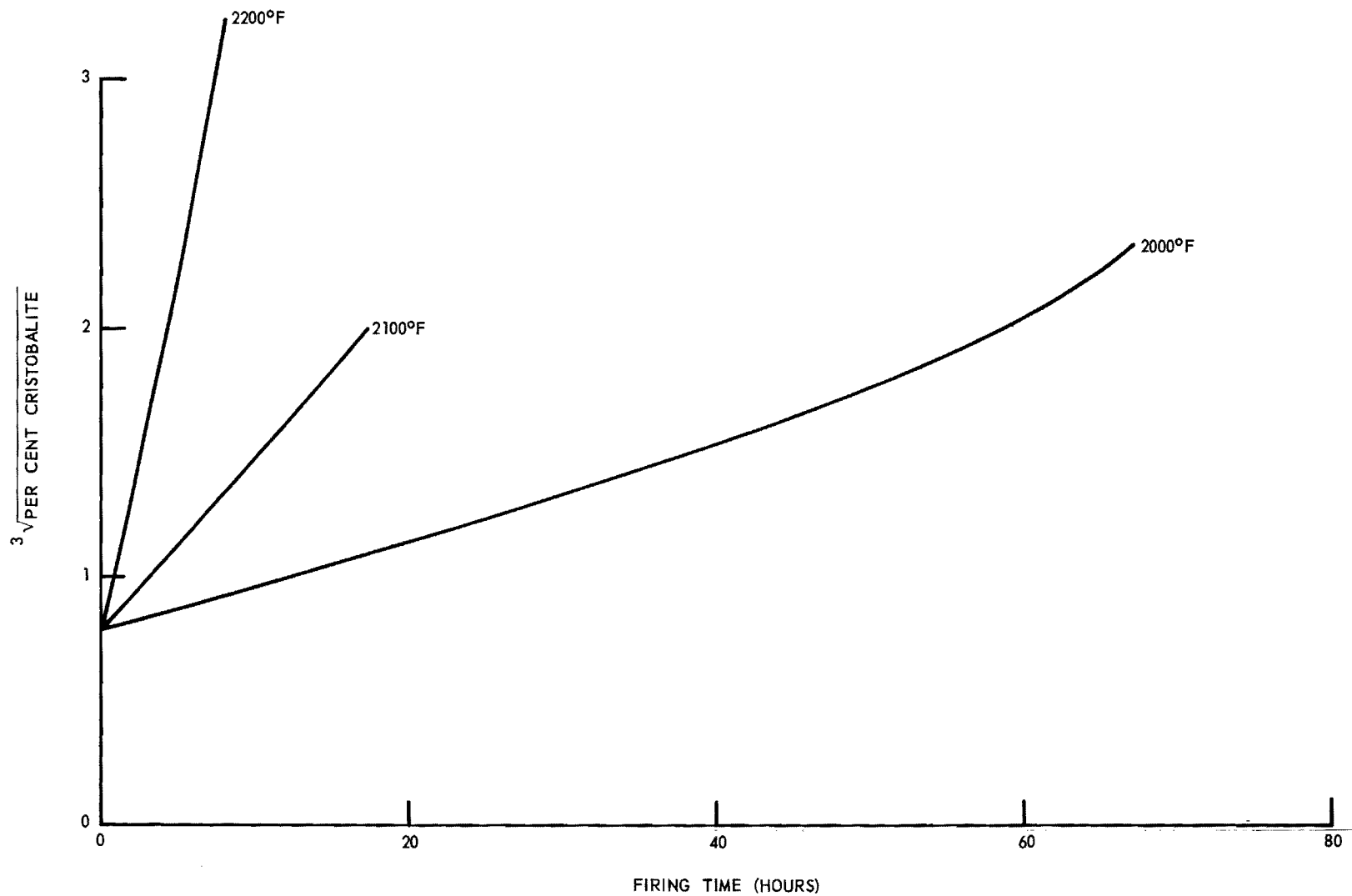


Figure 5. Cristobalite Content of Slip Cast Fused Silica Sintered In Steam Under a Pressure of One Atmosphere.

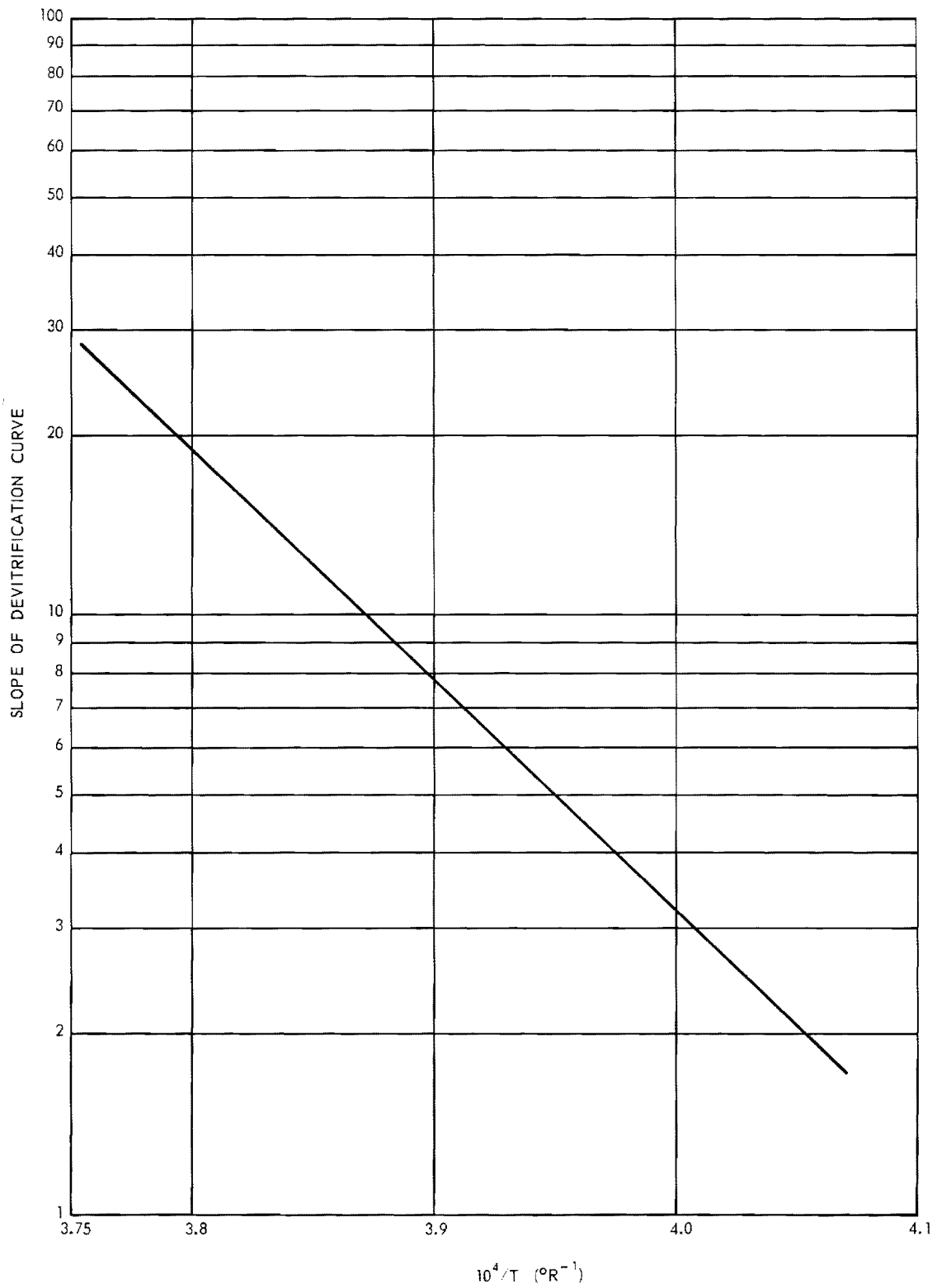


Figure 6. Arrhenius Plot for Devitrification of Slip Cast Fused Silica in One Atmosphere Absolute Steam.



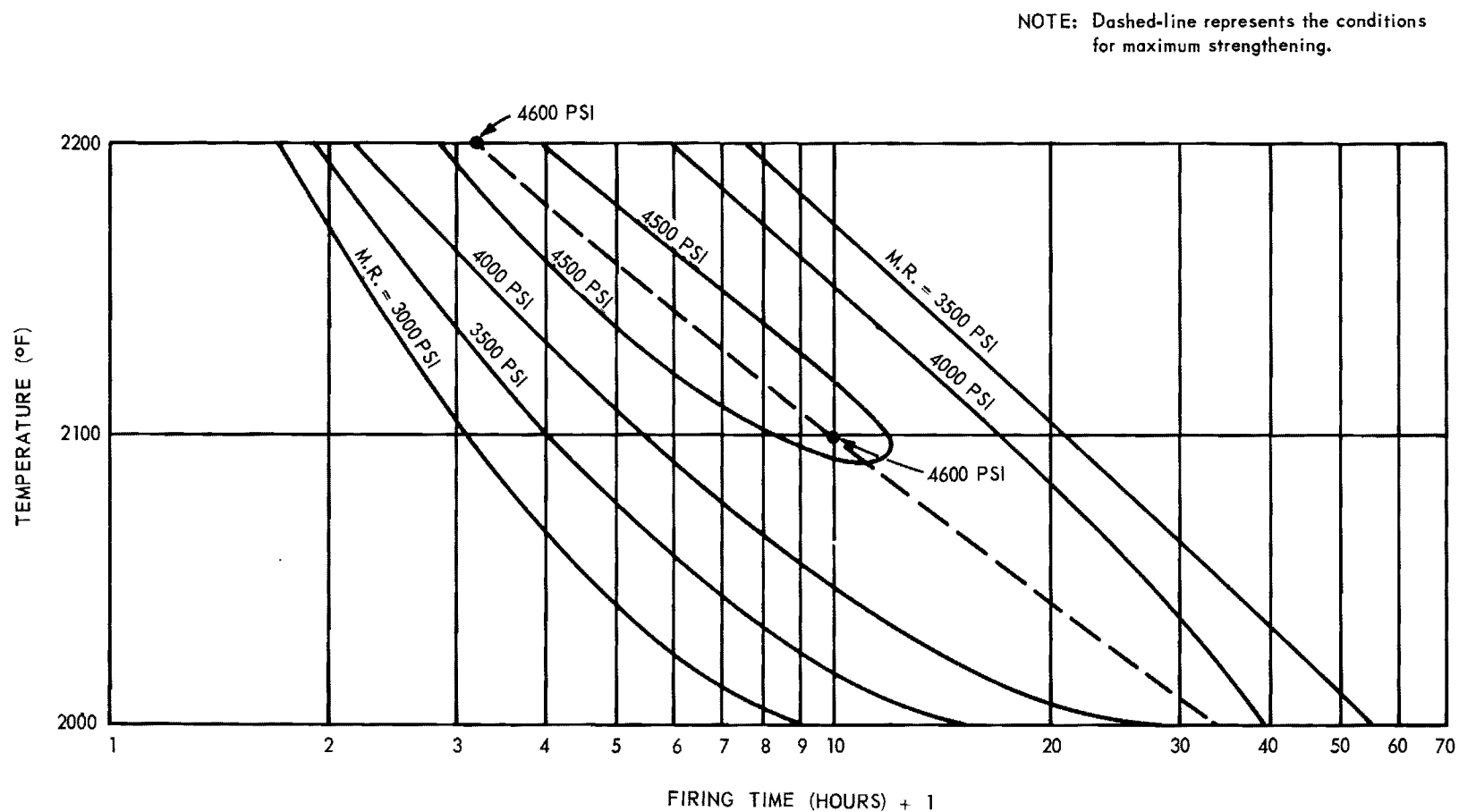


Figure 7. Modulus of Rupture Contour for Slip Cast Fused Silica Fired Under One Atmosphere of Steam.

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- 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.
- g) During firing, the steam pressure was maintained at two atmospheres absolute using a 15 psig "pop-off" valve placed at the end of the furnace opposite the water inlet.

The porosity, bulk density and apparent theoretical density of each fired bar were determined by air displacement. Following these measurements, the modulus of rupture of each bar was determined in three point loading by breaking once on a four inch span and, using the end pieces from the first break, twice on a two inch span.

Although data reduction for this study is not yet complete, the preliminary results of the strength and porosity determinations are shown in Figures 8 and 9. As a matter of interest, 2100° F strengthening curves are shown in Figure 10 for firing in air, one atmosphere steam, and two atmosphere steam.

3. Pressure-Vibration Casting

A further study was made of the effects of pressure application and mold vibration during casting of the fused silica slip. A set of 160 bars 3/4-in. in diameter by 5-5/8-in. long was cast in one piece molds using the graphite mold release. Internal pressures of 0, 20, 40, and 60 psig were placed on the casting slip and 60 cps axial vibrations of 0-, 0.010-, 0.012-, and 0.015-in. amplitude were applied. The castings were made in random order using a new mold for each specimen. The casting times were recorded. The bars were dried overnight in the molds, removed, air dried overnight, heated to 110° F for six hours and, finally, to 270° F for 16 hours. The porosity, bulk density, and apparent theoretical density of each bar were determined by

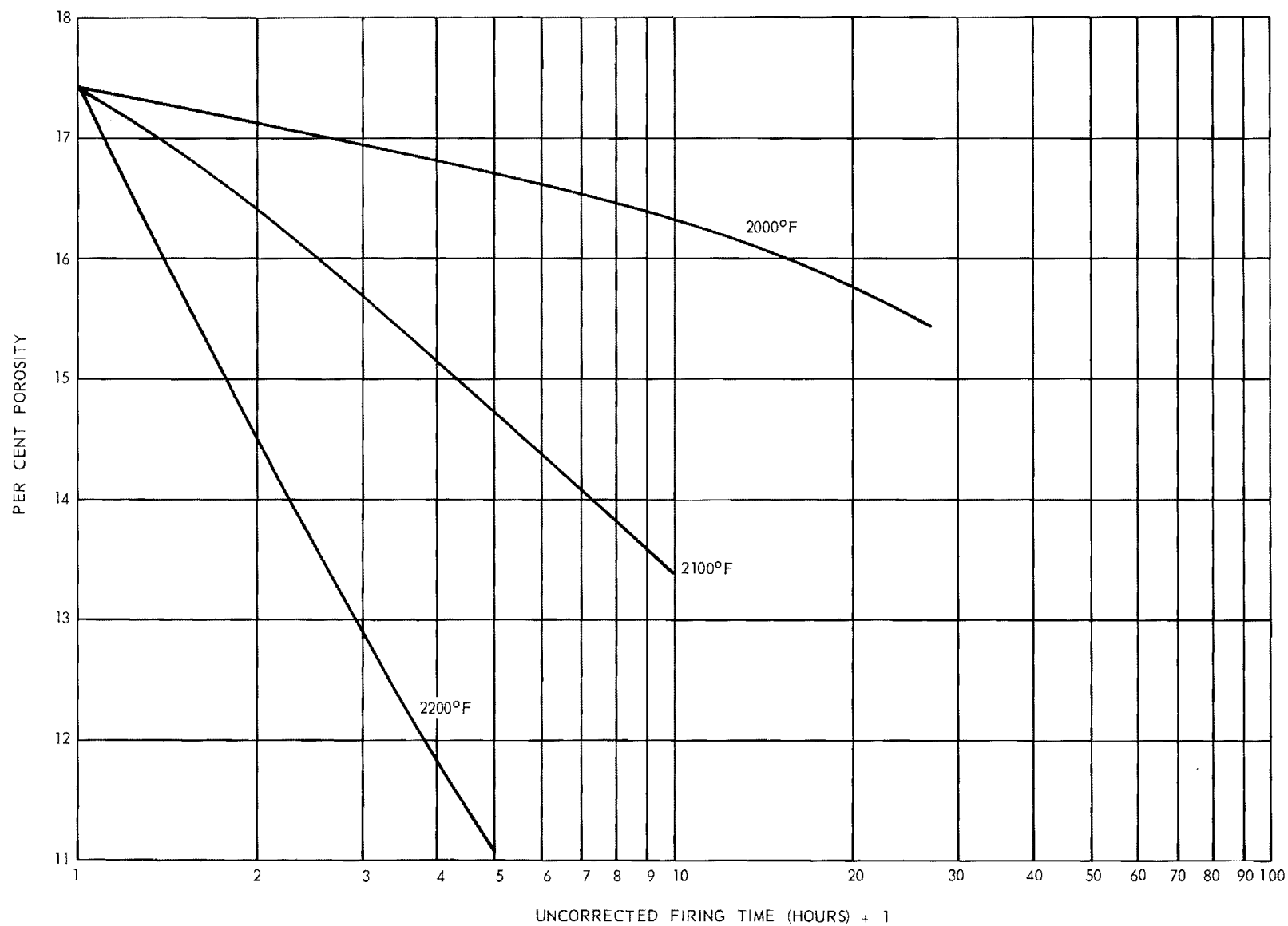


Figure 8. Porosity of Slip Cast Fused Silica Sintered in 2 Atmospheres of Steam.  
(Preliminary Data)

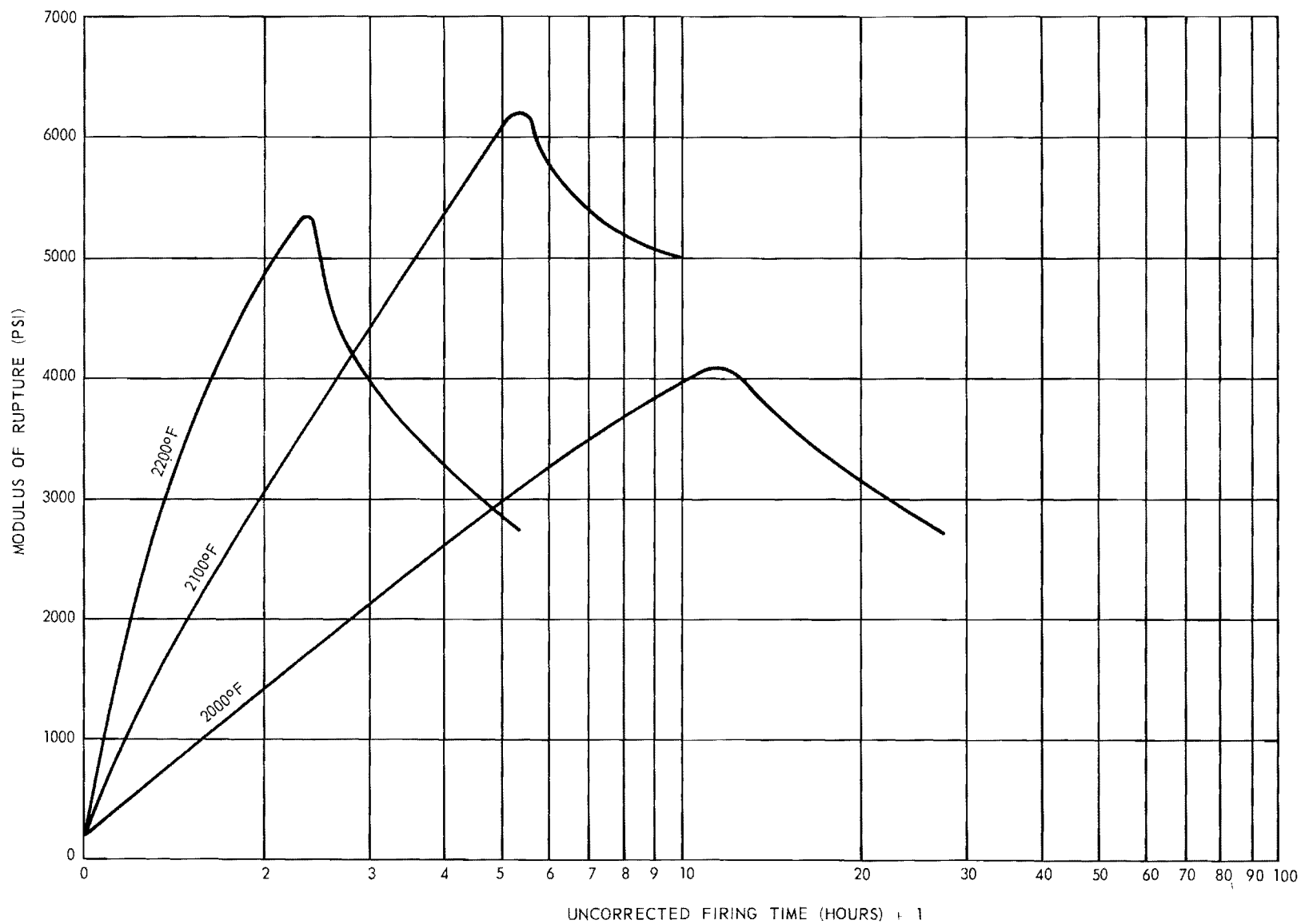


Figure 9. Modulus of Rupture of Slip Cast Fused Silica Sintered in 2 Atmospheres of Steam. (Preliminary Data)

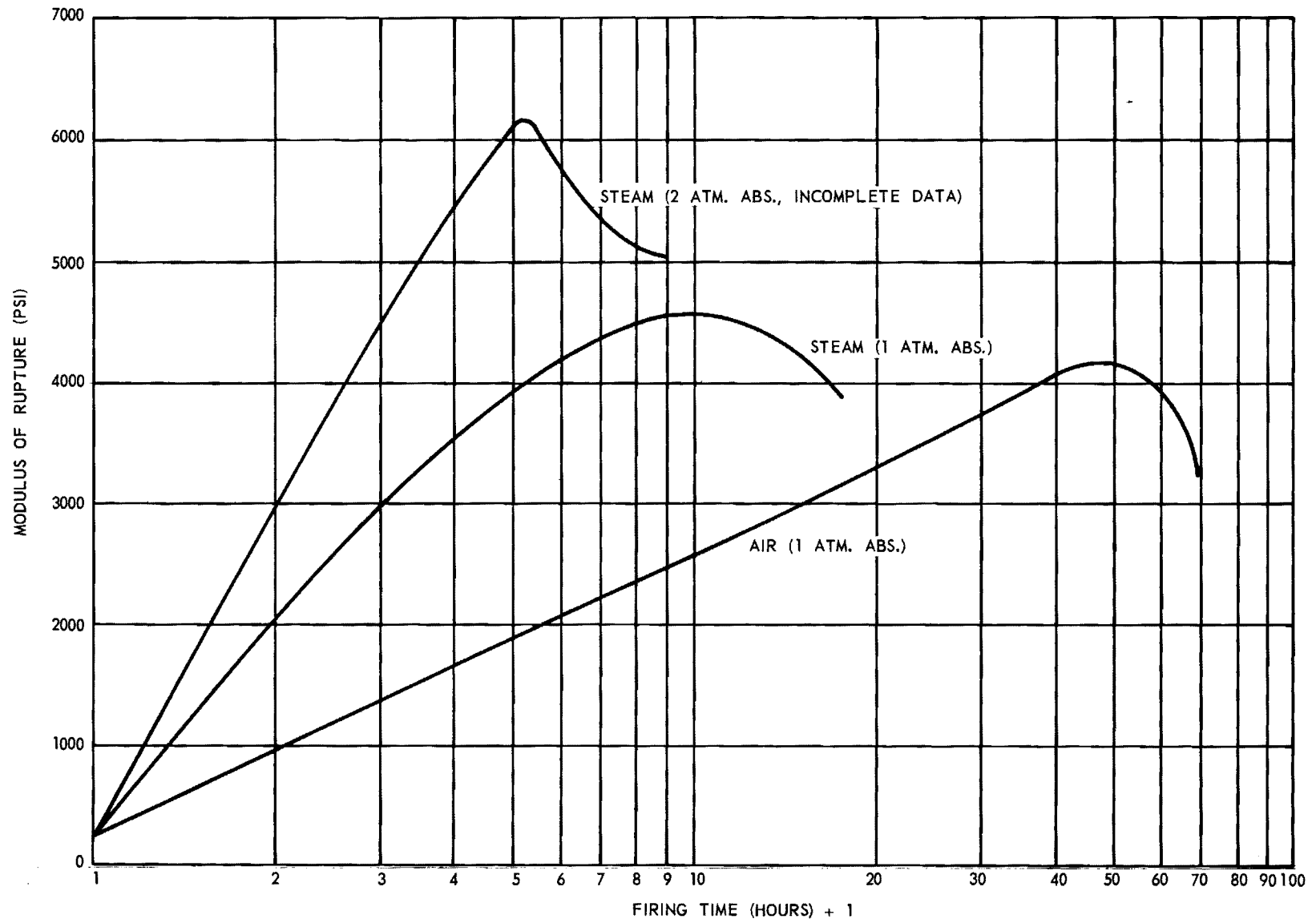


Figure 10. Strengthening Curves for Slip Cast Fused Silica Fired at 2100° F in Air and in Steam.

air displacement. The averaged bulk properties are shown in Table I.

In general, application of pressure is seen to produce a significant lowering of the casting time at the cost of a lower cast density. Vibration increases the cast density without strongly affecting the casting time. The strength of vibration available for the study was not sufficient to maintain the cast density at the zero pressure-zero vibration level with high casting pressures. The importance of this effect will be evaluated from modulus of rupture measurements now being made.

## B. Aluminum-Uranium Oxide Reactions

### 1. High Temperature X-ray System

A furnace was constructed to adapt the high temperature x-ray diffraction system to dynamic Al-U<sub>3</sub>O<sub>8</sub> 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<sub>α</sub> radiation is used.

The high temperature furnace is illustrated in Figures 11 and 12. It is a more refined version of a furnace used in earlier work on this project<sup>1</sup>. 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

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1. Progress Report No. 1, pp. 35-37.

TABLE I

BULK PROPERTIES OF FUSED SILICA  
SLIP CAST UNDER PRESSURE AND VIBRATION

<u>Pressure</u> (psig)	<u>Amplitude</u> <u>of Vibration</u> (in.)	<u>Approximate</u> <u>Casting Time</u> (Min.)	<u>Porosity</u> (%)	<u>Bulk</u> <u>Density</u> (gm/cc)	<u>Apparent</u> <u>Theoretical Density</u> (gm/cc)
0	0	150	17.8	1.854	2.26
0	0.010	150	17.6	1.849	2.24
0	0.012	150	16.4	1.879	2.25
0	0.015	150	15.8	1.890	2.24
20	0	33	18.0	1.853	2.26
20	0.010	33	17.6	1.846	2.24
20	0.012	33	17.7	1.843	2.24
20	0.015	33	17.8	1.858	2.26
40	0	25	17.8	1.848	2.25
40	0.010	25	17.7	1.848	2.25
40	0.012	25	18.1	1.841	2.25
40	0.015	25	17.9	1.845	2.25
60	0	17	18.2	1.846	2.26
60	0.010	17	18.2	1.837	2.25
60	0.012	17	18.4	1.843	2.26
60	0.015	17	18.2	1.849	2.26

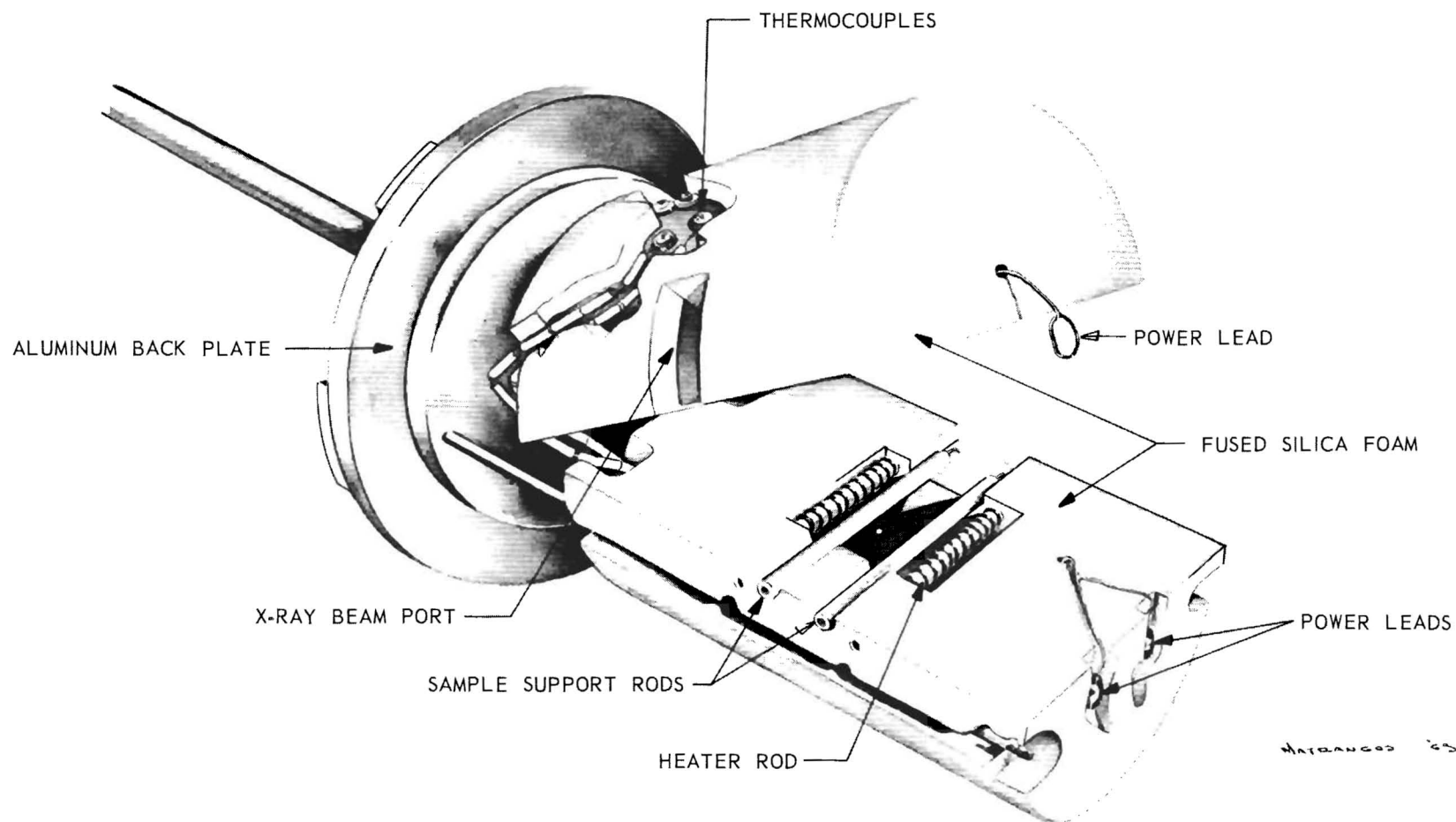
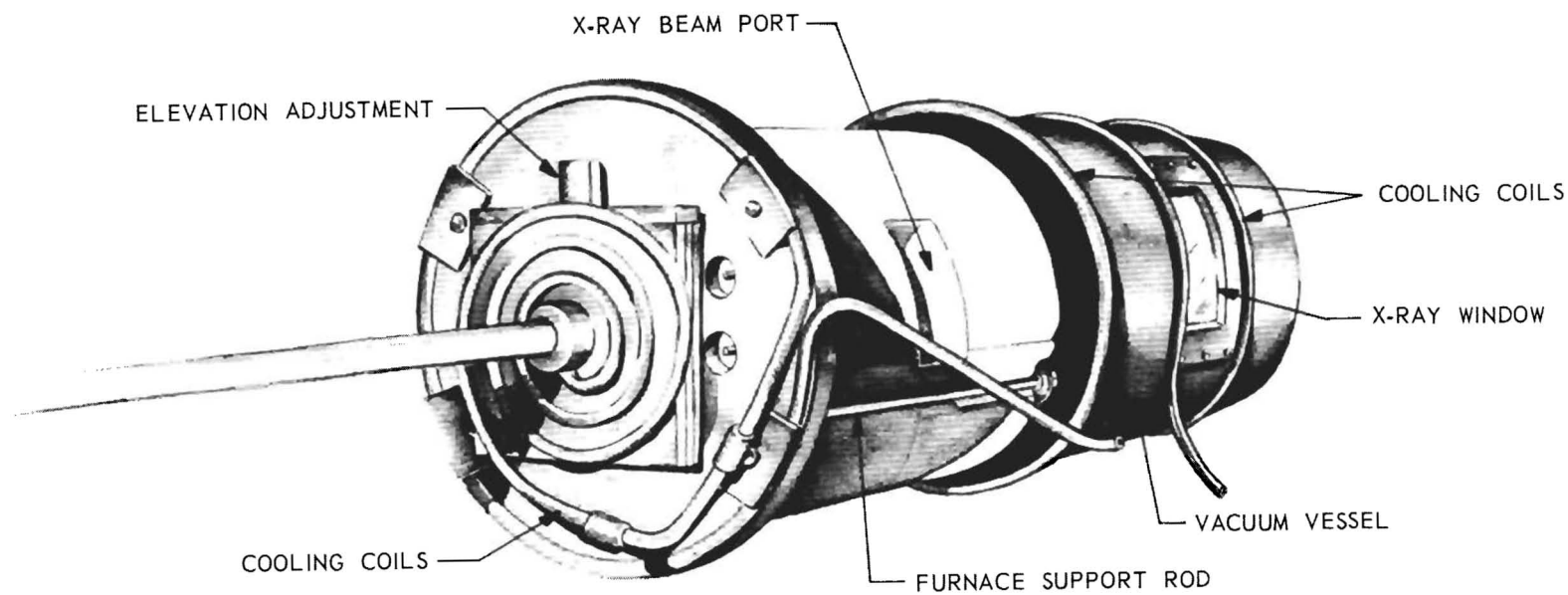


Figure 11. High Temperature X-ray Diffraction Furnace.





WATKINS 65

Figure 12. Rear View of High Temperature X-ray Diffraction Furnace Showing Vacuum Vessel.

vacuum glands in the aluminum end plate and brought by copper wire to the right end of the furnace body (see Figure 11), 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 13), and the other permits the temperature to be monitored by a potentiometer. The temperature can also be determined 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 11 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 0.0005-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 ( $2\theta$ ) of 0 to  $60^\circ$ , which is adequate for Al- $U_3O_8$  reaction product analyses. Provisions are made for adjustment of the sample elevation and orientation.

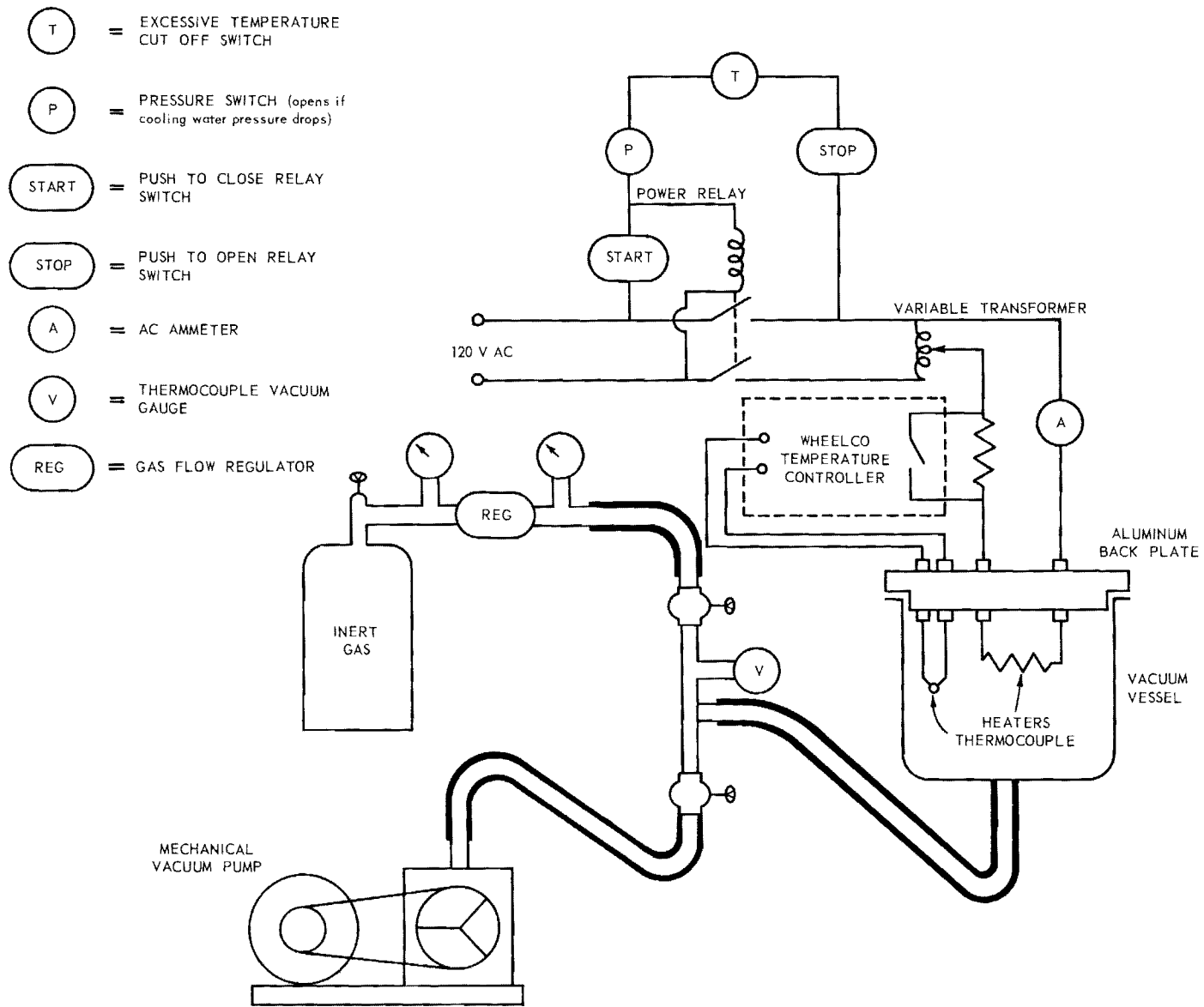


Figure 13. High Temperature X-ray Furnace Control System.

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Initial runs of ATR specimens were begun to test the performance of the x-ray system. These runs suggested minor system modifications which are currently being completed. The runs also indicated that thermal noise from the molten specimen will not be a problem.

### 2. DTA Testing

Attempts were begun to extend the DTA test to at least semi-quantitative analysis of the extent of reaction in heated Al-U<sub>3</sub>O<sub>8</sub> compacts. A series of samples was prepared from the rolled ATR fuel plate<sup>1</sup>. 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. Typical raw data for two groups of pellets heated to 1600 and 1800° F are shown in Table II.

Examination of the raw data shows that qualitative correlations among the various quantities measured do exist. For example, the specimens heated through the reaction exotherm show significant UAl<sub>4</sub> contents and a concomitant decrease in the aluminum DTA exotherm compared with the endotherm. In these specimens, the UO<sub>2</sub> content appears higher than that of the specimens not heated through the reaction exotherm. In spite of these consistent trends, discrepancies are noted. There is an apparent lack of quantitative correlation between the reaction exotherm peak areas and the x-ray data. Specimen 47-F, which shows the

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1. Quarterly Report No. 3, p 14.

TABLE II

## DTA AND X-RAY DATA FOR FIRED ATR SPECIMENS

Sample *	Weight (gm)	DTA Peak Area			X-ray Peak Area					
		Al Endotherm	Al Exotherm	Reaction Exotherm	U <sub>3</sub> O <sub>8</sub>			UO <sub>2</sub>		UAl <sub>4</sub>
		(in <sup>2</sup> )	(in <sup>2</sup> )	(in <sup>2</sup> )	21.5°	26°	34°	28.3°	55.6°	15.5°
39-16	3.97	2.35	1.25	---	0.32	0.58	0.54	0.09	0.07	0
40-16	3.78	1.65	1.36	---	0.43	0.88	0.72	0.15	0.04	0.02
41-16	3.51	1.64	1.22	---	0.41	1.00	0.74	0.15	0	0
42-16	3.80	1.80	1.32	---	0.34	0.74	0.69	0.13	0	0
44-F	3.52	2.14	0	0.61	0.62	0.66	0.39	0.80	0	0.11
45-F	3.41	1.92	0.32	0.85	0.38	0.48	0.39	0.62	0	0.12
46-F	3.84	2.40	0.17	0.90	0.43	0.50	0.26	0.56	0	0.09
47-F	3.48	2.55	0.19	0.87	0.70	0.78	0.56	0.92	0	0.24
48-F	3.41	2.12	0.50	0.72	0.66	0.84	0.51	0.84	0	0.19

\* -16 = Terminal DTA temperature of 1600° F

-F = Terminal DTA temperature above reaction exotherm peak (~1900° F).

largest concentration of  $\text{UAl}_4$  and  $\text{UO}_2$  and the strongest reaction exotherm (a consistent relationship) also perversely shows the greatest concentration of  $\text{U}_3\text{O}_8$  in the -F group.

The comparisons to be made are more readily seen from the reduced data of Table III. The arrangement of Table III should correspond roughly to increasing conversion of  $\text{U}_3\text{O}_8$ . A general, but by no means totally consistent or quantitative trend toward lower aluminum exotherm:endothrm 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-endothrm ratio obviously exists between the -16 and -F group as would be expected. The x-ray data show a trend toward higher  $\text{UO}_2$  contents in the more strongly reacted samples as well as a reasonable qualitative correspondence between high  $\text{UO}_2$  and high  $\text{UAl}_4$ . A possible explanation for the lack of correlation of  $\text{U}_3\text{O}_8$  with the reaction products and the reaction exotherm peak areas is apparent in the  $\text{U}_3\text{O}_8$  diffraction peak area ratios of Table III. The absence of constant area ratios indicates either significant matrix absorption differences, varying  $\text{U}_3\text{O}_8$  preferred orientation, or more likely, shifts in the oxide stoichiometry.

In view of the difficulties experienced with x-ray analysis for  $\text{U}_3\text{O}_8$ , 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  $\text{Al-U}_3\text{O}_8$  reaction. Such an approach could provide only rough accuracy

TABLE III  
REDUCED DATA FOR ATR SPECIMENS

Sample <sup>1</sup>	DTA Peak Areas		X-ray Peak Areas			
	Reaction Exotherm (in <sup>2</sup> /gm)	Al Cooling Exotherm Al Heating Endotherm	U <sub>3</sub> O <sub>8</sub> Area Ratio <sup>2</sup>		Total	
			26°	36°	UO <sub>2</sub> (in <sup>2</sup> )	UAl <sub>4</sub> (in <sup>2</sup> )
41-16	---	0.744	2.44	1.80	0.15	0
40-16	---	0.824	2.05	1.67	0.19	0.02
42-16	---	0.733	2.18	2.03	0.13	0
39-16	---	0.532	1.81	1.69	0.16	0
44-F	0.173	0.0	1.07	0.53	0.80	0.11
48-F	0.211	0.236	1.27	0.77	0.84	0.19
46-F	0.234	0.071	1.16	0.61	0.56	0.09
45-F	0.249	0.169	1.26	1.03	0.62	0.12
47-F	0.250	0.075	1.11	0.80	0.92	0.24

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

-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.

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

$$E = x\Delta h_f \frac{A_R}{A_M} \quad 2)$$

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.

The first problem apparent in this DTA calorimetry approach was, not surprisingly, selection of an appropriate standard material. With the rather unconventional application of DTA to high thermal conductivity materials, such as the ATR specimens, matching the thermal diffusivity of sample and standard becomes considerably more critical and more difficult.



The survey of standard materials<sup>1</sup> was extended to high aluminum test compacts. The result of this survey was that graphite should, in principle, be as satisfactory a standard as any other readily available inert material, at least for compacts of ATR composition.

A series of tests was begun to evaluate both the graphite standard and the DTA calorimetry approach. Several 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 the ATR fuel plate<sup>2</sup>.

Although only two tests have been made to date, the results are sufficiently interesting to be reported. Figure 14 shows DTA curves obtained with a graphite standard and with a pre-fired ATR standard. Neither curve provides a clear base line but this is to be expected from the mismatch in thermal diffusivity. No statement can be made from the graphite standard curve concerning low temperature reactions. The heating and cooling aluminum therms appear similar in both curves but the therms are, as would be anticipated, larger in the graphite curve. The reaction exotherms are much the same in both cases.

The data from the two graphite standard runs made to date are summarized in Table IV.

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1. Quarterly Report No. 2, p. 20.
  2. If the technique is successful, the standard and unknown need not be of similar size or shape.

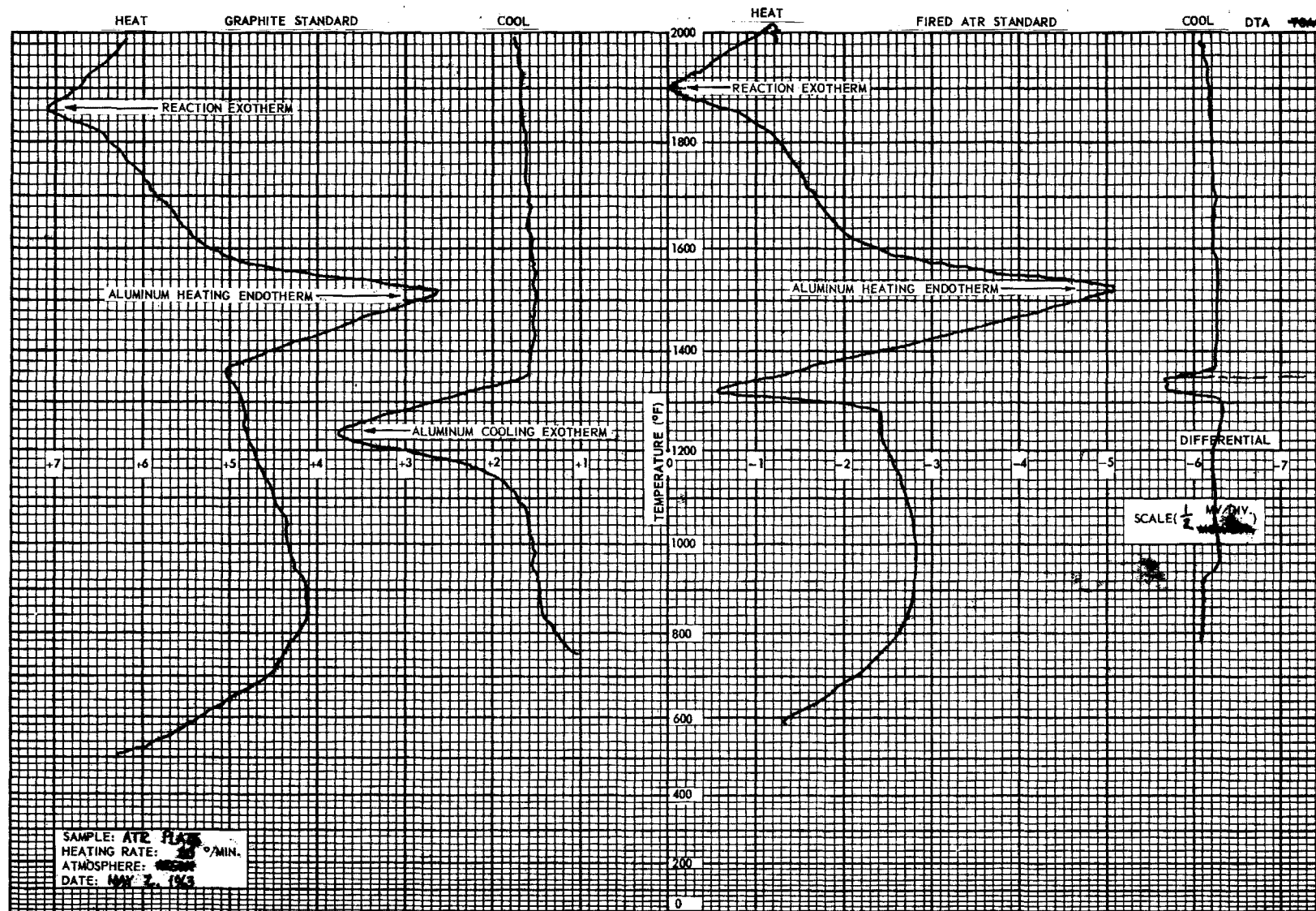


FIG 14

Figure 14. DTA Curves Run with Graphite and Fired ATR Standards.

TABLE IV  
INITIAL DTA CALORIMETRY RESULTS

	<u>Sample G-1</u>	<u>Sample G-2</u>
Sample Weight (gm)	3.86	3.81
Reaction Peak Temperature (°F)	1840	1850
Aluminum Melting Endotherm		
Peak Area (in <sup>2</sup> )	2.96	2.70
Aluminum Solidification		
Exotherm Peak Area (in <sup>2</sup> )	1.93	1.76
Apparent Aluminum Conversion (%) <sup>1</sup>	35	35
Reaction Exotherm Peak		
Area (in <sup>2</sup> )	1.01	0.75
Apparent Reaction Energy Release		
(Mw-sec/kg)	0.059	0.072
Theoretical Maximum Energy		
Release (Mw-sec/kg)	0.62	
Theoretical Maximum Aluminum		
Conversion (%)	28.4	
1. Assuming % conversion = $(1 - \frac{\text{Exotherm Area}}{\text{Endotherm Area}}) 100$		

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The principal difficulty encountered in making the calculations for Table IV 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 in Table IV 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.

#### IV. DISCUSSION

The analysis of the early devitrification in slip cast fused silica seems to correlate well with the observed cristobalite content. This analysis and the corresponding analysis of the conditions for maximum strengthening offer possibilities for investigation of the sintering behavior of slip cast fused silica which were not previously available. Studies of the kinetics and activation energies of the solid state transport phenomena, devitrification, sintering shrinkage, strengthening and porosity change, are now possible. Comparison of the parameters characterizing these processes should shed light on the mechanisms of silica sintering.

Steam firing of slip cast fused silica continues to be most interesting from both a fundamental and an applied standpoint. The practical advantages of more rapid processing and better material properties are apparent though the limitations of the method are not yet in sight. From the fundamental viewpoint the obvious conclusion of a different effect of steam on the bulk flow and devitrification processes offers great potential for further investigations. It is entirely possible that the science of silica processing will be completely altered by further studies in this field.

Although not yet complete, the current results of the pressure-vibration casting experiment are quite pleasing. The significant decrease in casting time with pressure application will permit fabrication of much more homogeneous castings provided the sintering properties are not drastically altered.

Techniques for applying DTA to the determination of aluminum conversion and energy release in reacting Al-U<sub>3</sub>O<sub>8</sub> compacts will obviously require much refinement prior to use. The results of the first studies are not at all discouraging and no reason is apparent as to why the method should not prove successful. The advantages of such a technique should not be overlooked with respect to kinetics studies of high U<sub>3</sub>O<sub>8</sub> composites. While the dynamic x-ray diffraction technique appears more suitable for the slow reaction in ATR compacts, higher U<sub>3</sub>O<sub>8</sub> contents will probably produce reaction kinetics beyond the time response capacity of the x-ray system. In this case, DTA may offer an alternate approach to the kinetics measurements. The financial advantages of internally calibrated DTA calorimetry are obvious for Al-U<sub>3</sub>O<sub>8</sub> compacts of any composition.

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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. Paul Boland	Group Leader
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
Mr. W. M. Linstrom	Technician
Mr. P. S. Matrangos	Technician
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Submitted by:

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VI. APPENDICES



APPENDIX A

ANALYSIS OF EARLY CRISTOBALITE GROWTH IN SILICA

The devitrification of fused silica is well known to proceed from the surface inward. The initial stages should thus involve growth of cristobalite about isolated surface sites of nucleation. If any cristobalite is present in the starting slip, it will also tend to appear at the surface since, during grinding, the cristobalite points should act as stress concentrators. These stress concentration points should undergo fracture during grinding, producing particles in which the cristobalite appears principally on the surface, where it can serve as nucleation points for devitrification. Considering the nuclei to be hemispherical points sunk into the fused silica particle surface, the rate of cristobalite growth should depend directly on the nucleus surface area available for further growth, at least until the surface is covered with cristobalite. As a result

$$\frac{dx}{d\theta} = C_1 (2\pi r^2) \quad 3)$$

where  $x$  = cristobalite concentration

$\theta$  = time

$C_1$  = constant of proportionality

$r$  = average growth nucleus radius.

Since

$$x = \frac{\text{Mass of Cristobalite}}{\text{Mass of Bar}}$$

the concentration is

$$x = \frac{\frac{2}{3} \pi r^3 \rho_c n}{M_B}$$

where  $\rho_c$  = cristobalite density

$n$  = number of nuclei in sintering bar

$M_B$  = mass of sintering bar.

If the number of growth nuclei is assumed constant

$$x = C_2 r^3$$

and

$$r = C_3 x^{1/3}$$

Substituting into Equation 3.

$$\frac{dx}{d\theta} = C_4 x^{2/3}$$

and integrating

$$x^{1/3} = C_5 \theta + x_0^{1/3}. \quad 4)$$

Equation 4 shows that a plot of the cube root of the cristobalite concentration as a function of time should be linear in the early stages of devitrification and that the intercept of the line should be the initial cristobalite concentration in the slip.

If the temperature effects are included in the early devitrification process, since the devitrification is thermally activated, Equation 3 becomes

$$\frac{dx}{d\theta} = C_1 e^{-\frac{E}{RT}} (2\pi r^2) \quad 5)$$

where E = activation energy

R = gas constant

T = sintering temperature

and, after the same manipulation as before,

$$x^{1/3} = C_5 e^{-\frac{E}{RT}} \theta + x_0^{1/3}. \quad 6)$$

Equation 6 shows that the plot of  $x^{1/3}$  against  $\theta$  will have a slope of

$$M = C_5 e^{-\frac{E}{RT}}. \quad 7)$$

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A plot of the log of the devitrification curve slope,  $M$ , against the reciprocal absolute sintering temperature should thus give a straight line of slope  $-\frac{E}{R}$ . From such an Arrhenius plot, the devitrification activation energy may be calculated.

APPENDIX B

ANALYSIS OF MAXIMUM STRENGTH CRITERIA IN SILICA

In conjunction with the discussion in Section III, assume a small, but fixed, amount of cristobalite to be detrimental to the strength of the silica. Assume further that only one basic mechanism is operative for initial devitrification, so that we can write:

$$\frac{dx}{d\theta} = Kf(x) \quad 8)$$

where:  $x$  = cristobalite content

$\theta$  = firing time

$K$  = rate constant

$f(x)$  = a function (unknown to us) whose form depends on the governing devitrification mechanism; i.e., depending on the order of the reaction, whether or not the reaction is autocatalytic, etc.

Then, since the process is a thermally activated one, in the case of varying temperature, we have

$$\frac{dx}{d\theta} = Ae^{-\frac{E}{RT}} f(x). \quad 9)$$

where  $E$  is the activation energy,  $R$  is the gas law constant,  $T$  is the absolute temperature and  $A$  is a constant.

Rearranging equation 9) and integrating:

$$\int_{x_0}^{x_i} \frac{dx}{f(x)} = Ae^{-\frac{E}{RT}} \cdot \theta_i \quad 10)$$

where  $\theta_i$  is the time required for the cristobalite content to increase from its initial value  $x_0$  to the critical value  $x_i$ . Since the left hand side of equation 10) is equal to a constant, say  $C$ , we can write

$$\ln \theta_i = \ln A' + \frac{E}{RT} \quad 11)$$

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where  $A' = C/A$ . Equation 11) shows that if a plot is made of  $\ln \theta_1$  versus  $1/T$ , a straight line with slope  $\frac{E}{R}$  should be obtained.

VII. PRIOR REPORTS

Previous reports issued under this contract are:

1. Monthly Letter Reports Nos. 1 - 52, Issued each month since December 1958.
2. Progress Report No. 1, August 1959. Issued as ORO-209 by OTS, Department of Commerce.
3. Progress Report No. 2, Part 1, August 1960, Issued as ORO-325 by OTS, Department of Commerce.
4. Progress Report No. 2, Part 2 (Declassified), August 1960.
5. Progress Report No. 3, August 1961.
6. Quarterly Report No. 1, April 1962.
7. Summary Report No. 1, July 1962.
8. Quarterly Report No. 2, October 1962.
9. Quarterly Report No. 3, January 1963.

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QUARTERLY REPORT NO. 5

PROJECT NO. B-153

MATERIALS FOR HIGH TEMPERATURE  
NUCLEAR ENGINEERING APPLICATIONS

By J. D. Fleming, J. W. Johnson,  
Paul Boland, and S. H. Bomar

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

Contract No. AT-(40-1)-2483

1 October

Engineering Experiment Station  
**GEORGIA INSTITUTE OF TECHNOLOGY**  
Atlanta, Georgia

1963



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

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June 1, 1963 to October 1, 1963

Quarterly Report No. 5, Project No. B-153

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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.

This report covers the period from June 1, 1963 to October 1, 1963.

## I. INTRODUCTION

During recent years, fused silica has assumed the status of an engineering material. With the development of slip-casting techniques, the fabrication cost has been decreased substantially and much more complex shapes are feasible. Slip-cast fused silica is currently being used in many critical applications ranging from brazing and heat treating fixtures for supersonic aircraft components to prototype radomes for hypersonic missiles. The properties which have made slip-cast fused silica suitable for these uses combine with good radiation resistance to recommend it for use in high temperature nuclear applications. One object of Project B-153 is the development and compilation of data sufficient to evaluate slip-cast fused silica for such nuclear applications.

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  $U_3O_8$ . Since Al- $U_3O_8$  dispersions are in common use as reactor fuels, the results of this study are obviously of interest in hazards evaluation. Several special studies of Al- $U_3O_8$  dispersions are included in the program to assist hazards evaluation.

## II. SUMMARY

Determinations were made of the elevated temperature tensile strength of slip-cast fused silica using a brittle ring test. In order to avoid casting flaws in individually cast rings, specimens were sawed from 12-inch long cylinders cast while being rotated.

Rings fired to optimum room temperature strength at firing temperature-time combinations of 2133° F for 19 hours, 2166° F for 8-1/2 hours, and 2200° F for 3-1/3 hours showed essentially the same response to increased testing temperatures. The tensile strength increased roughly linearly from approximately 3100 psi at room temperature to approximately 8100 psi at 2100° F.

Rings fired for various times at 2200° F showed similar responses to elevated testing temperatures. All rings increased in tensile strength with increased testing temperature to 2000° F. The increase was generally more noticeable in the rings fired for longer times during maturation. The ratio of the strength at 2000° F to the strength at room temperature was 1.63 for rings fired for 0.5 hour and 2.75 for rings fired for 5 hours.

The activation energies for early cristobalite growth were determined for firing under one atmosphere of steam and air. In air firing, the activation energy was 150 kcal. per gram mole and in steam the energy was 100 kcal. per gram mole.

Etching techniques were studied for phase identification in Al-U<sub>3</sub>O<sub>8</sub> dispersions. Two methods were found to show promise. Etching for 12 hours in a Syntron polisher filled with magnesium oxide slurry removes the aluminum alloy matrix, leaving behind the uranium oxides and aluminum oxide. Stereo-

micrography of the etched specimens reveals the oxide macrostructure.

A 0.5 per cent HF solution was found to cause differential staining of the U-Al intermetallic compounds in  $\text{Al-U}_3\text{O}_8$  dispersions when applied by swabbing for 40 seconds. Preliminary studies indicated that the stain colors were stable and reproducible. Electron microprobe analyses were carried out to correlate the phase compositions with the stain colors. Although the data from these studies are not yet completely reduced, preliminary results indicated that the 0.5 per cent HF etchant colors  $\text{UAl}_4$  blue while  $\text{UAl}_3$  is outlined but not colored.

ATR  $\text{Al-U}_3\text{O}_8$  dispersions sag tested under a static pressure differential at 1380, 1710, and 1860° F were examined after HF etching. In the two lower temperature runs, which produced sag at 0.6 and 0.9 psi respectively, an oxide-free alloy exuded under pressure, producing porosity in the dispersion area. The exuded area was free of uranium oxides and a sharp line of demarcation was apparent between the dispersion and exudate areas. Both areas showed evidence of reaction since a blue-staining phase, tentatively identified as  $\text{UAl}_4$ , was present. The 1860° F test failed to produce sag under an applied stress of 4 psi, the maximum obtainable in the apparatus. No exudation occurred. Extensive reaction was apparent. The  $\text{U}_3\text{O}_8$  was essentially completely reacted and massive amounts of blue-staining and light staining intermetallic compounds, tentatively identified as  $\text{UAl}_4$  and  $\text{UAl}_3$  respectively, formed in the alloy matrix.

III. EXPERIMENTAL PROGRESS AND DISCUSSION

A. Slip-Cast Fused Silica

1. Elevated Temperature Tensile Strength

Determinations were made of the tensile strength of slip-cast fused silica at elevated temperatures. In view of the strong increase of the strength with temperature and the inherent difficulties in axial tensile testing of ceramics, the Bortz ring test was used.<sup>1</sup> The ring stress constant used was obtained from Bortz's theoretical curve which was verified in a brief series of experiments.

The individual molds used to cast the rings in previous work were found to result in considerable variation in casting and firing characteristics of the rings. In addition, since the inner surface of the ring was formed against a non-porous mandrel and since the tensile break in the ring test originates at this surface, some doubt was evident that the "breaking fiber" was formed by casting rather than sedimentation. Dye penetrant tests indicated that the incidence of casting flaws was much higher at this surface than in other portions of the ring.

In order to minimize the adverse effects of the casting procedure, an alternate method was used in this series of tests. Fused silica cylinders with a nominal wall thickness of 3/4-inch were drain-cast in 3-inch inside diameter, 6-inch outside diameter plaster molds 12-inches long, using Keltex mold release. The molds were held horizontal and rotated at 36 rpm during casting. The molds were kept full of slip during casting by means of a

---

<sup>1</sup>Bortz, S. A. and Lund, H. H. "The Brittle Ring Test," pp. 383-406, Mechanical Properties of Engineering Ceramics, Interscience Publishers, Inc., New York (1961).



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reservoir connected to the casting cavity through a swivel joint. Five hours proved to be the required casting time.

The castings were air dried in the molds overnight, removed, dried to constant weight at 130° F, and dried at 230° F for 16 hours. After being dried, the silica cylinders were bisque-fired at 1800° F for two hours and diamond-sawed to thicknesses of 0.75- to 0.95-inches depending on the planned testing temperature. After being sawed, the rings were dried at 230° F for at least three hours and fired in a bottom loading Globar furnace. Firings were made at three optimum points, 2133° F for 19 hours, 2166° F for 8-1/2 hours, and 2200° F for 3-1/3 hours. In order to define the influence of firing conditions on the elevated temperature strength, additional 2200° F firings were made for 1/2, 2, 5, and 8 hours.

The following testing procedure was used:

1. The ring was placed in the testing furnace pre-heated to the desired testing temperature, during which the furnace cooled slightly.
2. Five minutes after the furnace returned to the testing temperature, the ring was stressed to fracture.

Strength determinations were made at room temperature, 400, 800, 1200, 1600, and 2000° F for each of the firing conditions. Bisque-fired rings were also tested at room temperature. Ten replicates were tested for each datum point.

The strength variation with temperature is shown in Figure 1 for the optimum fired rings. As was expected, the three optimum firing conditions

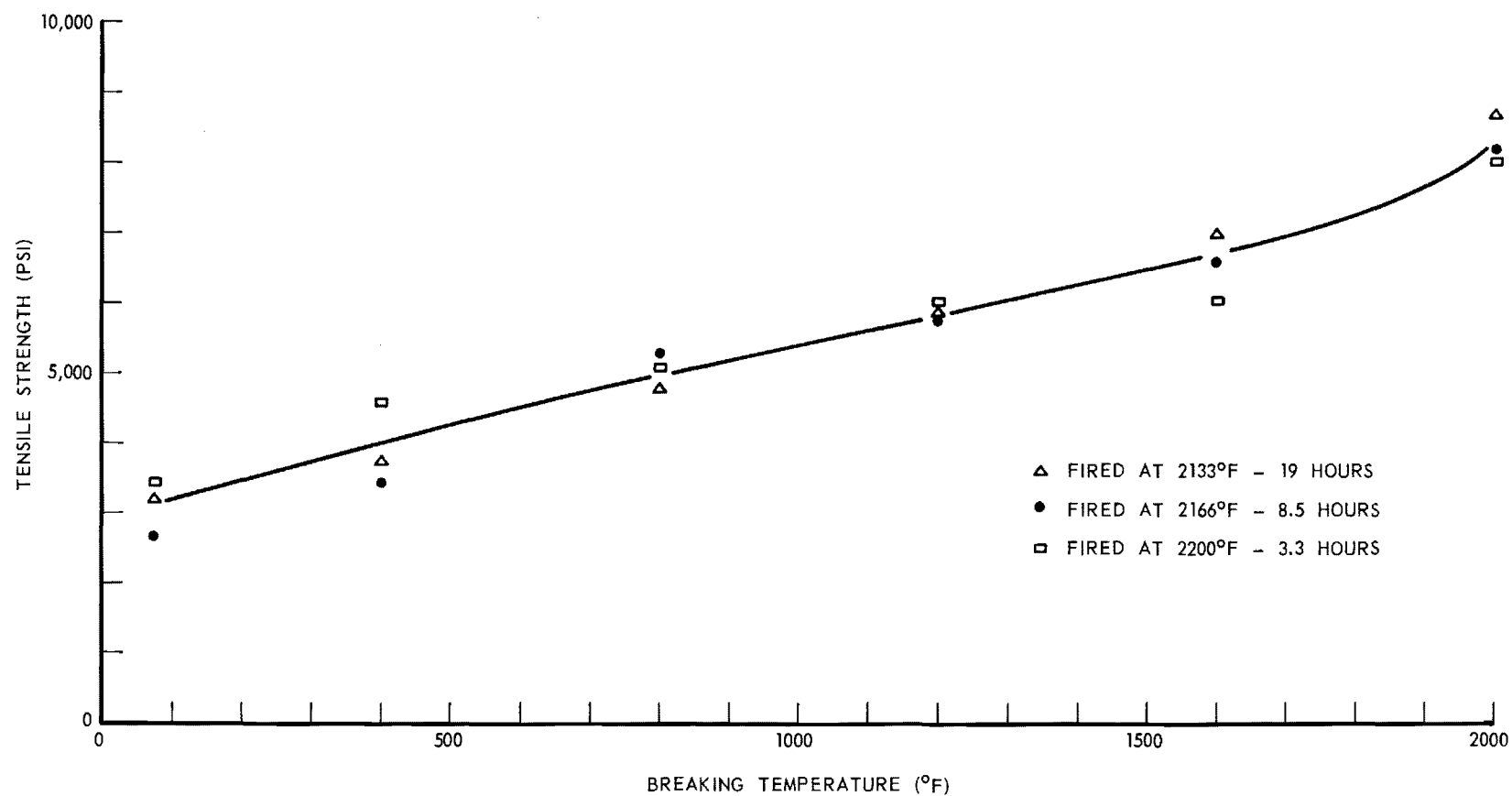


Figure 1. Elevated Temperature Tensile Strength of Optimum-Fired Slip Cast Fused Silica.

yielded essentially the same results.

The firing condition-testing temperature profile for the 2200° F firings is shown in Figure 2. Increased testing temperature produced increased tensile strength in all cases but the increase was much greater with increasingly severe firing during fabrication. The increase is presumably due to increased plasticity at elevated temperature and to partial healing of flaws generated by the rapid post-firing air quench.

Since confidence limits were excluded from the figures in order to avoid obscuring the curves, a summary of the statistical data is given in the Appendix for the tests.

## 2. Activation Energy For Steam and Air Firing

X-ray diffraction cristobalite analyses were completed for the majority of the runs made in air at 2000, 2100, 2133, 2166, 2200, and 2300° F. Several analyses were also made for samples fired at 2000, 2100, and 2200° F in steam under one atmosphere total pressure. These data were reduced according to the analysis of early cristobalite growth in silica which was discussed in a previous report.<sup>1</sup> This analysis indicated that the cristobalite content during the early stages of devitrification should follow a cubic time variation. Treatment of the air and steam firing data in this fashion gave very satisfactory results. Arrhenius plots of the slopes of these curves are shown in Figures 3 and 4. From the slopes of the Arrhenius plots, activation energies for devitrification were found to be 150 kcal. per gram mole for firing in one atmosphere of air and 100 kcal. per gram mole for firing in one atmosphere of steam. These results are consistent with indications obtained

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<sup>1</sup>Quarterly Report No. 4, pp. 39-41.

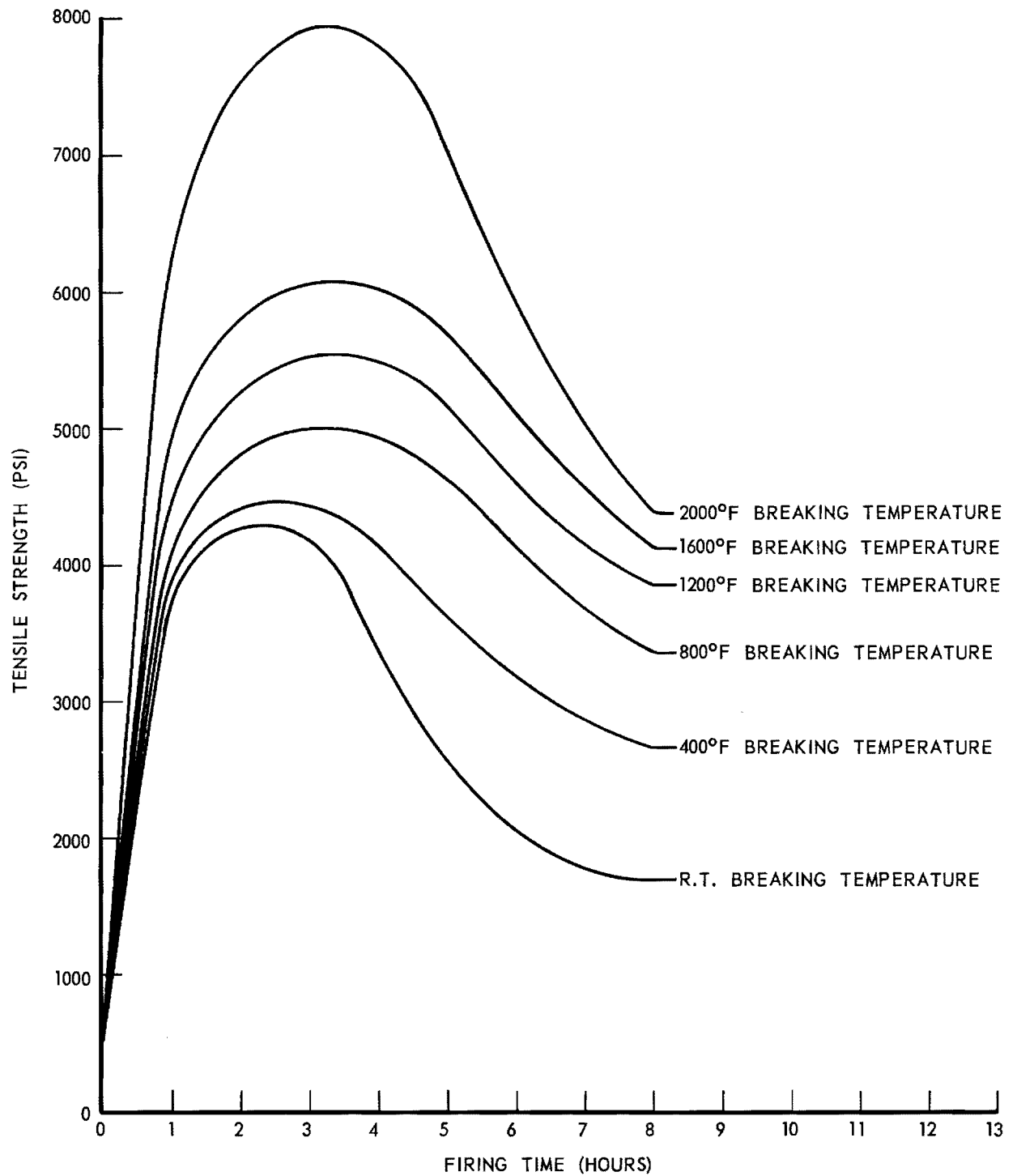


Figure 2. Elevated Temperature Tensile Strength of Slip Cast Fused Silica Fired at 2200° F.

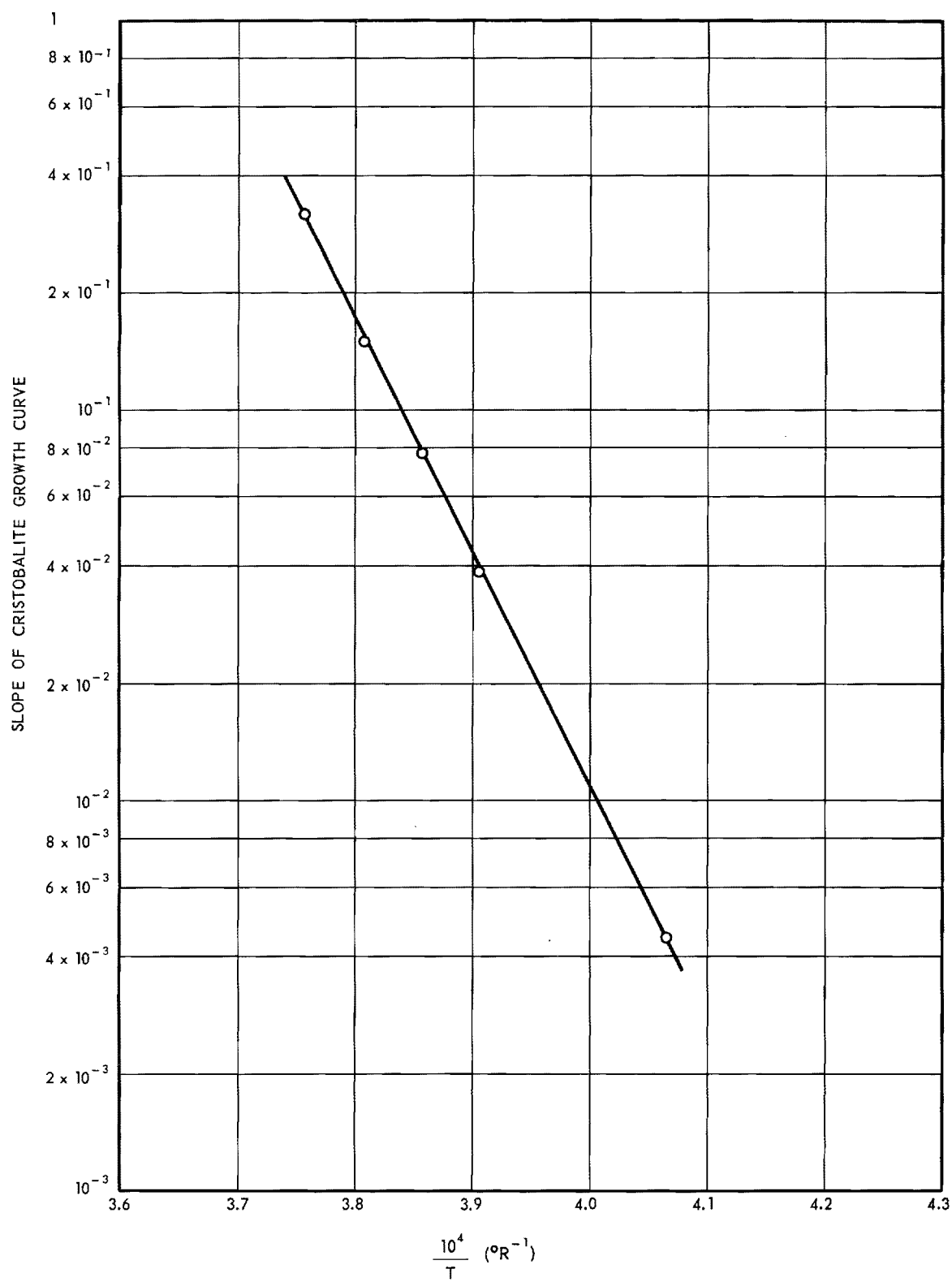


Figure 3. Arrhenius Plot for Early Cristobalite Growth in 1 Atmosphere Air Fired Slip Cast Fused Silica.

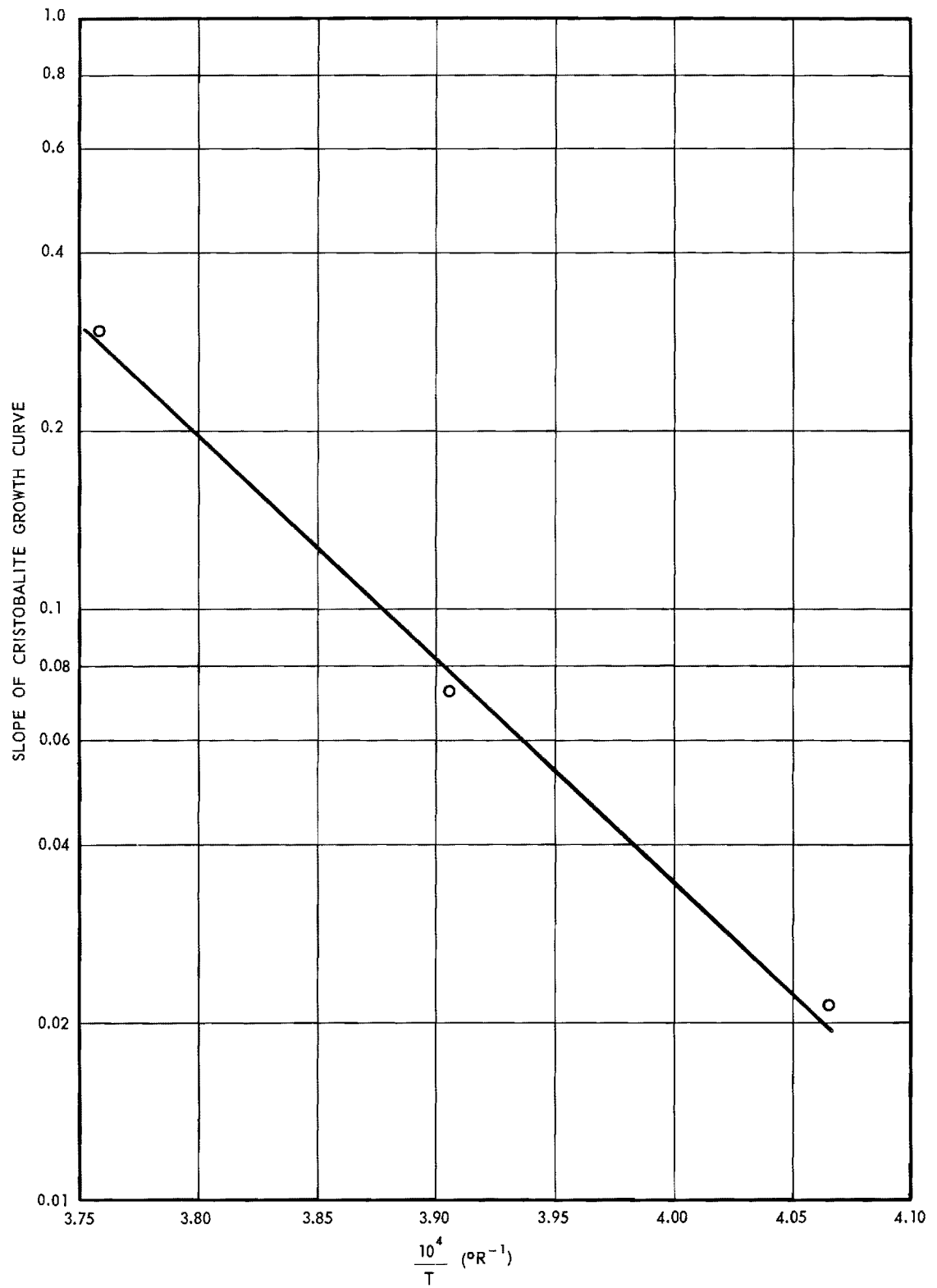


Figure 4. Arrhenius Plot for Early Cristobalite Growth in 1 Atmosphere Steam Fired Slip Cast Fused Silica.

in previous work, both on this project and by outside agencies, which indicates that steam does decrease the energy barrier for devitrification.

## B. Al-U<sub>3</sub>O<sub>8</sub> Interactions

### 1. Etching Studies

In order to provide a basis for metallographic identification of the phases in reacted Al-U<sub>3</sub>O<sub>8</sub> compacts, an investigation was made of the effects of various etching reagents on fired ATR compacts. Two etching techniques were found to show interesting possibilities. The first consists of immersion etching in a slurry of magnesium oxide on a Syntron polisher for approximately 12 hours. The basic solution resulting from slaking of the oxide results in removal of the aluminum matrix alloy and outlines the structure of the aluminum oxide, UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub> remaining behind. Stereophotomicrographs of such samples will be included in future reports.

The second etching reagent is 0.5 per cent HF in water, applied by swabbing for approximately 40 seconds. This etching technique was found to stain the intermetallic phases in the samples different colors. In order to investigate the reproducibility of this staining, one sample was stained, photographs were made, and the sample was repolished and restained. Identical color staining patterns were obtained in both the first and second etch.

To determine the phases corresponding to the stain colors, selected areas were subjected to electron microprobe analysis through the cooperation of the General Electric Nuclear Materials and Propulsion Operation. Figure 5 shows the location of the areas subjected to microprobe analysis. Figures 6 through 8 show micrographs of the particular particles studied.

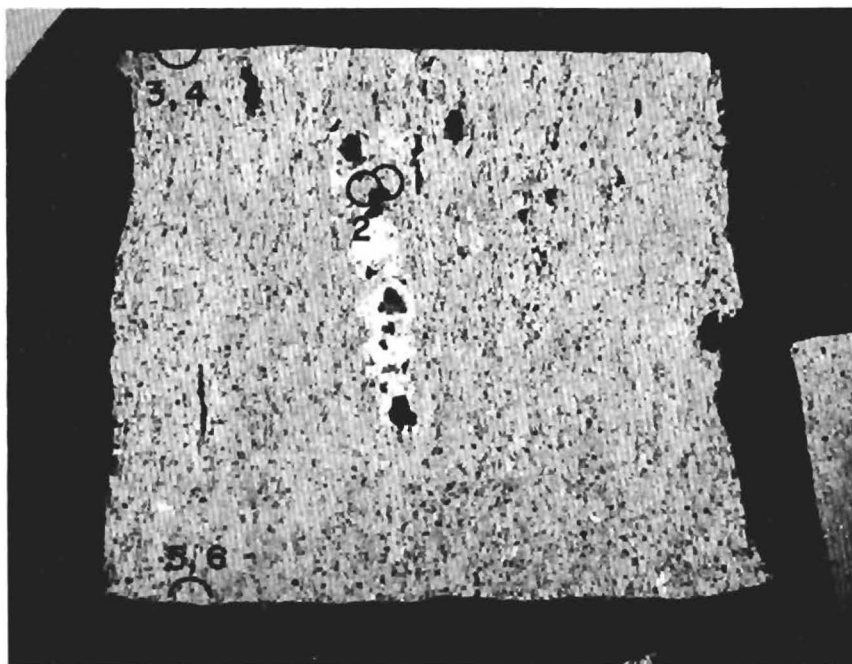
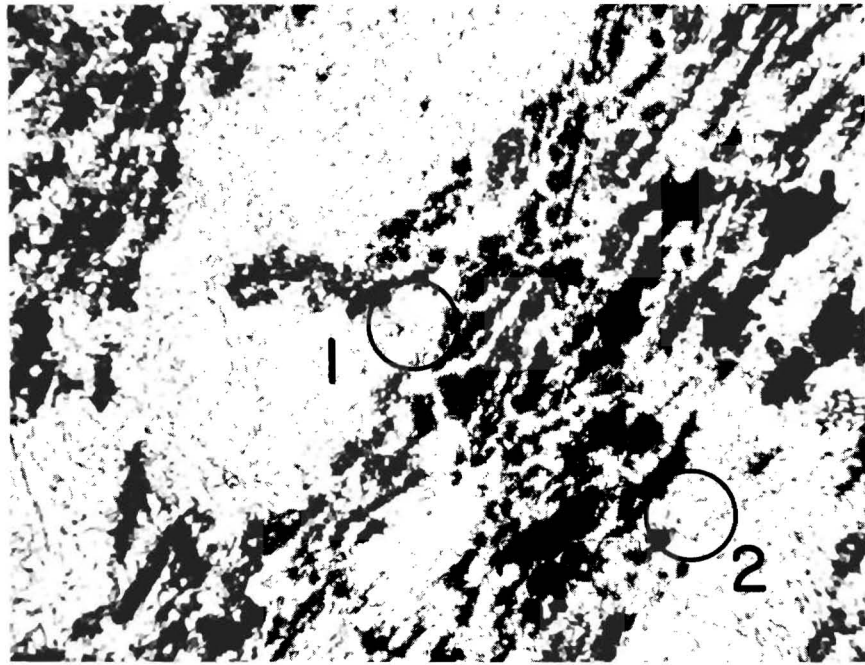
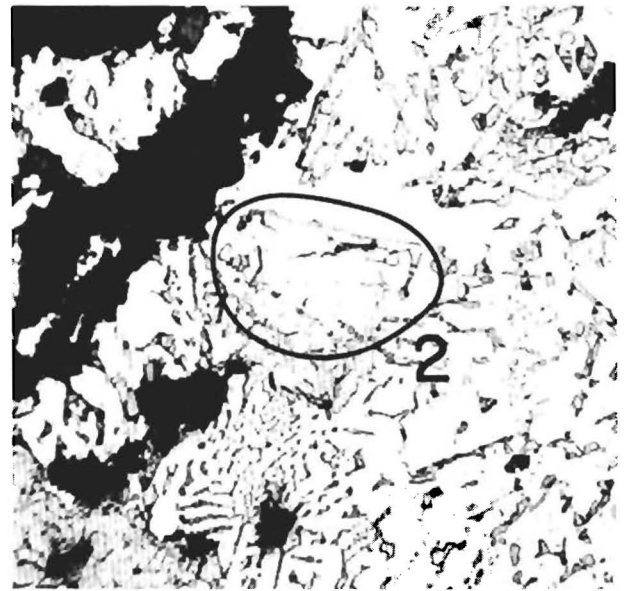
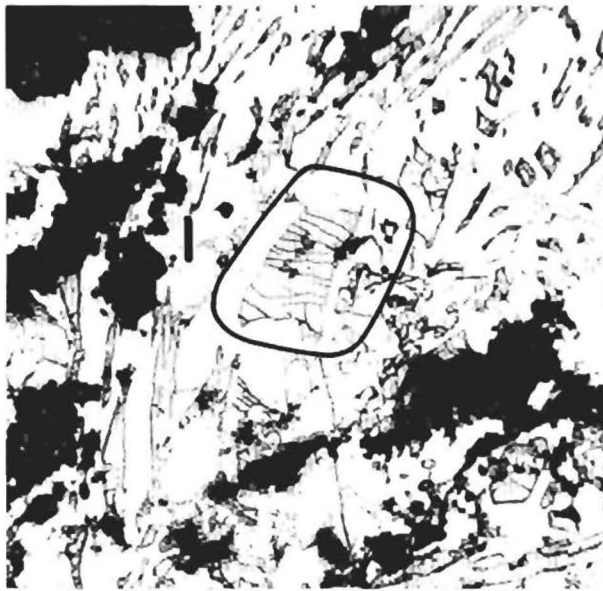


Figure 5. Location of Areas Subjected to Electron Microprobe Analysis (Approximately 7x).



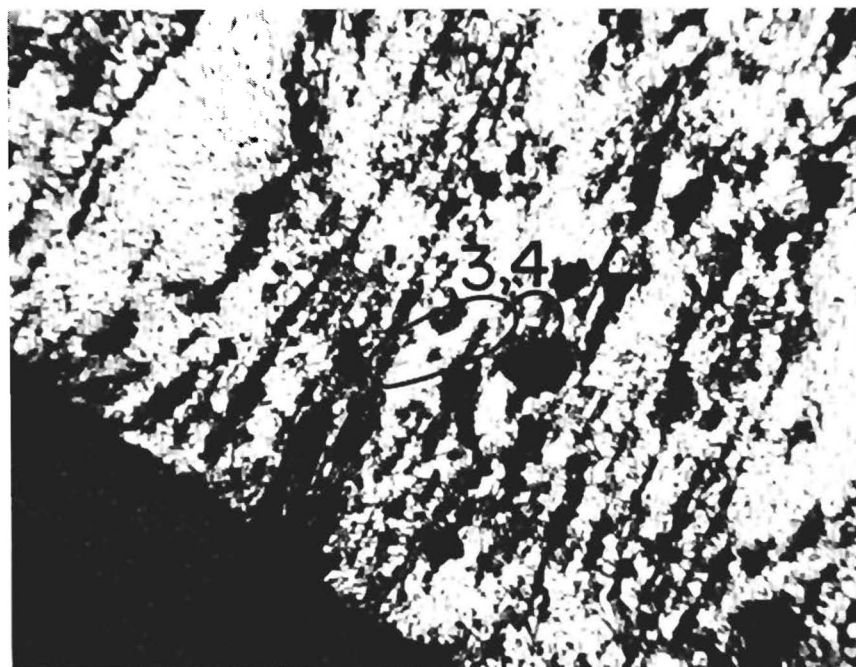


a. 62x

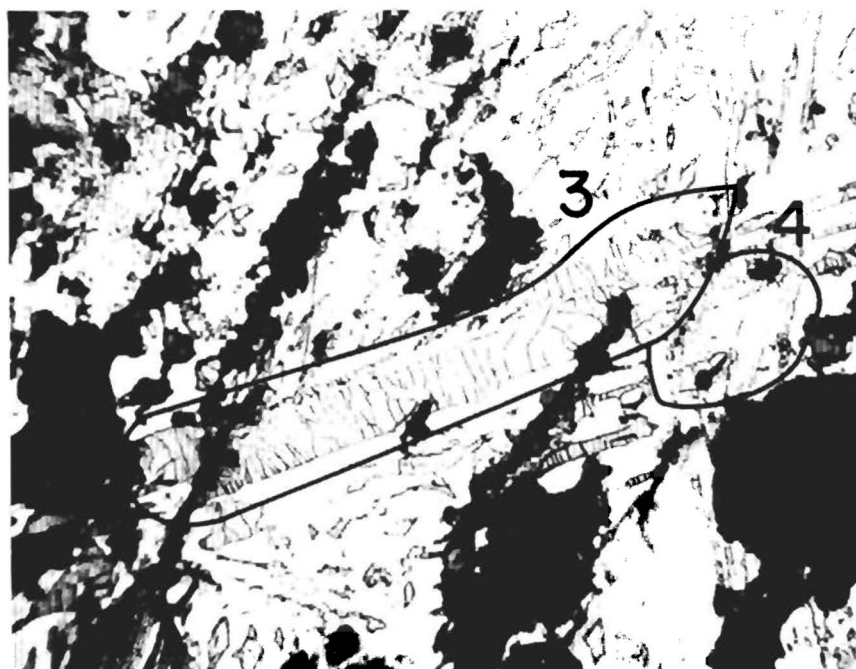


b. 250x

Figure 6. Electron Microprobe Particles 1 and 2, Etched in 0.5% HF

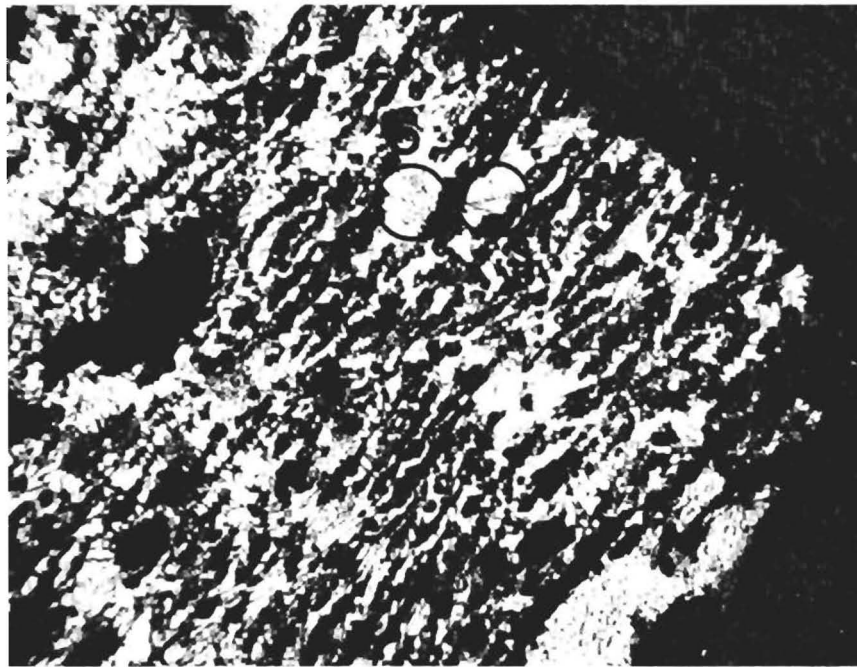


a. 62x

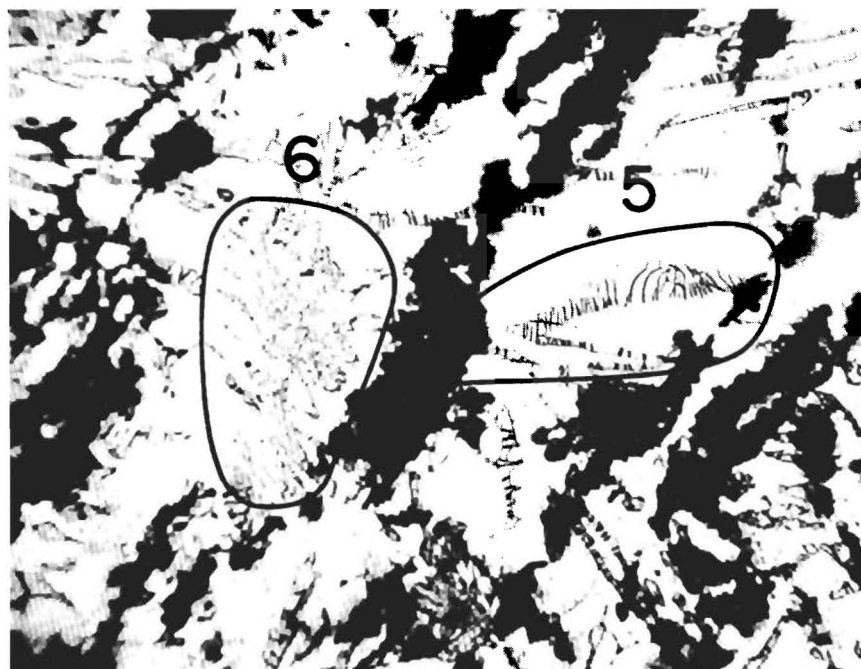


b. 250x

Figure 7. Electron Microprobe Particles 3 and 4, Etched in 0.5% HF.



a. 62x



b. 250x

Figure 8. Electron Microprobe Particles 5 and 6, Etched in 0.5% HF.

While the data from the analytical study have not been completely reduced, it appears from ratios of the uranium contents that particles 1, 3, and 5 are the same phase,  $UAl_4$  and particles 2, 4, and 6 are the same phase,  $UAl_3$ . The phases tentatively identified as  $UAl_4$  stain a blue color under the 40 second swab with 0.5 per cent HF while the particles identified as  $UAl_3$  do not stain to any great extent. Prolonged etching stains  $UAl_4$  particles very dark blue, passing into brown, while the  $UAl_3$  particles become yellow and pitted.

Further studies are planned to determine more completely the reproducibility, specificity, and stability of the HF stain colors. These studies will be made using several different alloy compositions to investigate the interfering effects, if any, of the various intermetallics.

## 2. Pressure Rupture of ATR Specimens

In Summary Report No. 2, descriptions were given of a brief series of tests in which ATR specimens were ruptured under a pressure differential in both the prefired and fired conditions. This study was extended and complete metallographic examinations were made.

Figure 9<sup>1</sup> shows the microstructure of the annealed dispersion before testing.

Figure 10 shows a sample, originally 93 mils thick, which sagged under an applied pressure differential of 0.6 psi at a temperature of 1380° F. Figure 11 shows the microstructure of the line of demarcation between the exuded metal area and the original sample area. Figure 12 shows the unetched and etched microstructures of the original sample area. Figure 13 shows the unetched and etched microstructures of the exuded metal area.

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<sup>1</sup>For convenience, Figures 9-20 are grouped together beginning on page 19.

Figure 14 shows a sample, originally 90 mils thick, which sagged under an applied pressure differential of 0.9 psi at a temperature of 1710° F. Figure 15 shows a micrograph of the line of demarcation between the original sample and the exuded metal structure. Figure 16 shows the unetched and etched structures in the original sample area. Figure 17 shows the unetched and etched structures in the exuded metal area.

Figure 18 shows a sample, originally 85 mils thick, which failed to sag under an applied pressure differential of 4 psi, the maximum obtainable in the apparatus, after firing at a temperature of 1860° F. Figure 19 shows the microstructure of the sample and Figure 20 shows the unetched and etched microstructures at higher magnification.

A comparison of Figures 10 and 14 shows that the deformation is grossly similar in both cases although the amount of exudate is greater in the higher temperature specimen. Internal porosity is apparent in both cases. At 1380° F, the porosity is perhaps more concentrated proximal to the exudate while, at 1710° F, the porosity seems to be greater in the areas distal to the exudate. The existence of the porosity could be explained in terms of the aluminum oxide substructure previously postulated<sup>1</sup> and observed in the magnesia-etched specimens to be reported later. Porosity should also result from the volume decrease accompanying reduction of the  $U_3O_8$ , as confirmed by the existence of substantial porosity without gross metal flow in the reacted specimen, Figure 18. The differences in exudate volume and porosity location in Figures 10 and 14 are probably due to the decrease in the alloy viscosity at the higher temperature.

---

<sup>1</sup>Summary Report No. 2

The existence of a bridging substructure is also supported by the sharpness of the lines of demarcation shown in Figures 11 and 15. Transport of metal into the exudate region disturbed the original oxide distribution little, if any, in either case.

In the original sample region, the changes observed in Figures 12, 16, and 20 consist principally of the development of increased porosity and the formation of U-Al intermetallics. The porosity increase is probably due to volume reduction through reaction and, in the lower temperature samples, metal exudation under the pressure differential. Since the alloy matrix is fluid at the testing temperature, formation of such voids would appear to imply the presence of internal gases. Although this would not be surprising, the porosity distribution, particularly in the 1860° F specimen, indicates that more detailed consideration is necessary for a complete explanation. One further factor which influences the appearance of presumed voids is the fact that the  $\text{UO}_2$  produced in the reduction tends to be granular and easily removed during mechanical polishing, thus giving a false indication of porosity.

The intermetallic phase in both the original sample and exuded metal regions of the lower temperature specimens, Figures 12, 13, 16, and 17, is entirely blue-staining  $\text{UAl}_4(?)^1$  upon 0.5 per cent HF etching. Particularly in the case of the 1380° F specimen, this provides support for the tentative identification of this phase as  $\text{UAl}_4$  by electron microprobe analysis.

A material balance for the ATR dispersion shows that

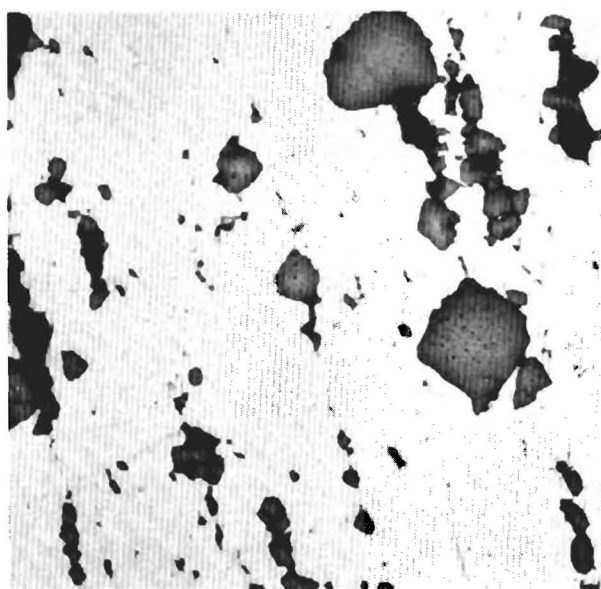
$$C_{\text{U}_3\text{O}_8} = \frac{2.29 x_{\text{U}}}{1 - 0.799 x_{\text{U}}} \quad 1)$$

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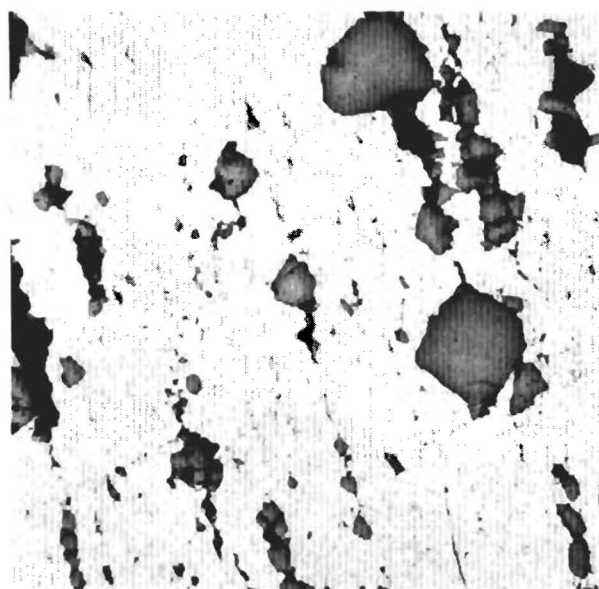
<sup>1</sup>The (?) notation is used to designate tentative identification.



a. Unetched, 62x



b. Unetched, 250x



c. Etched in 0.5% HF, 250x

Figure 9. Annealed ATR Dispersion Before Sag Testing.

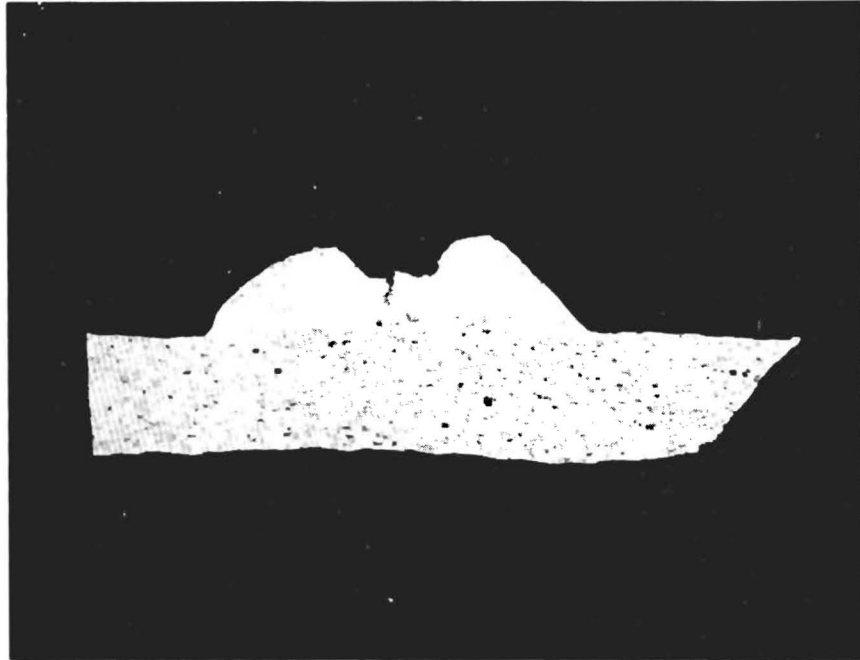


Figure 10. ATR Dispersion Sag Tested at  $1380^{\circ}$  F (7x).



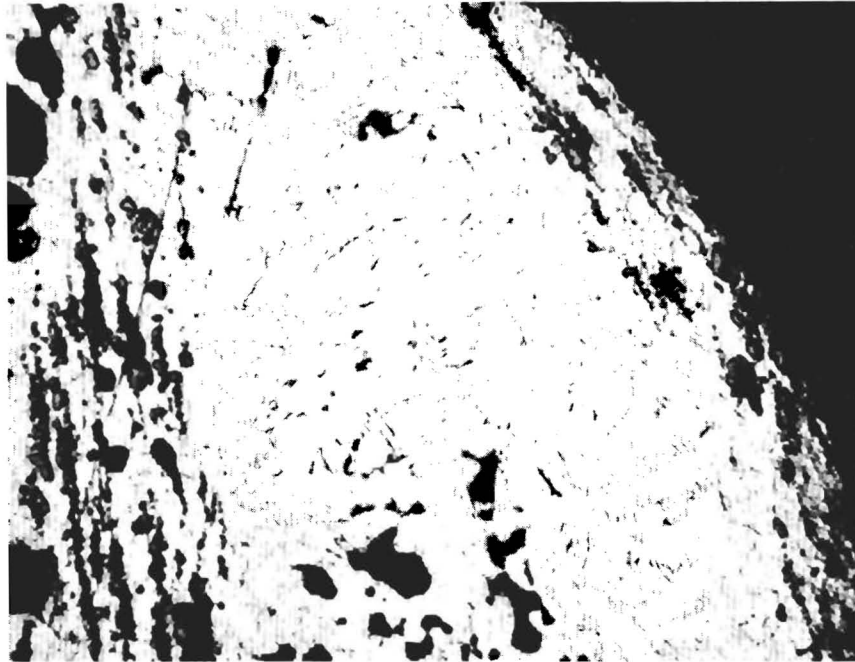
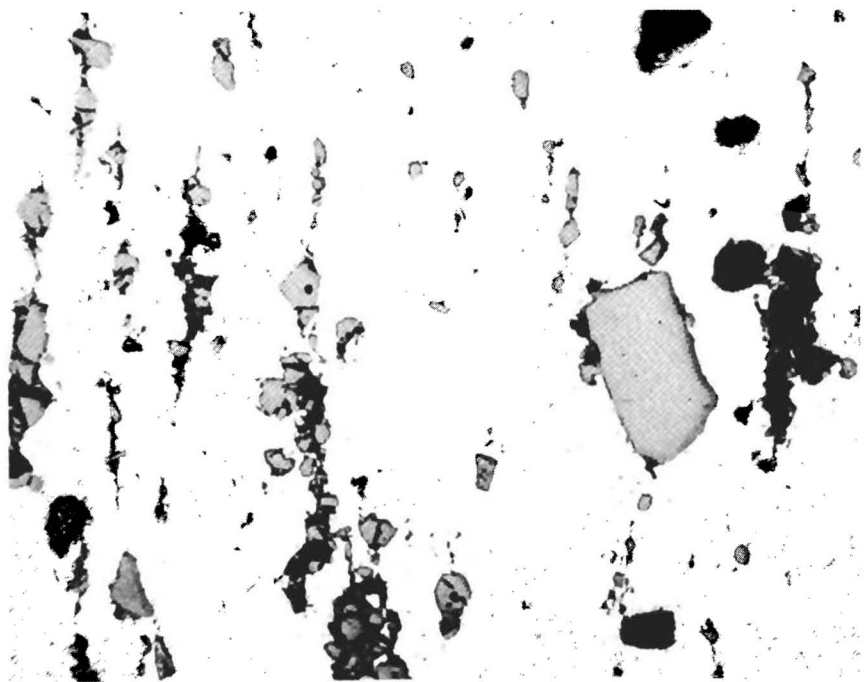
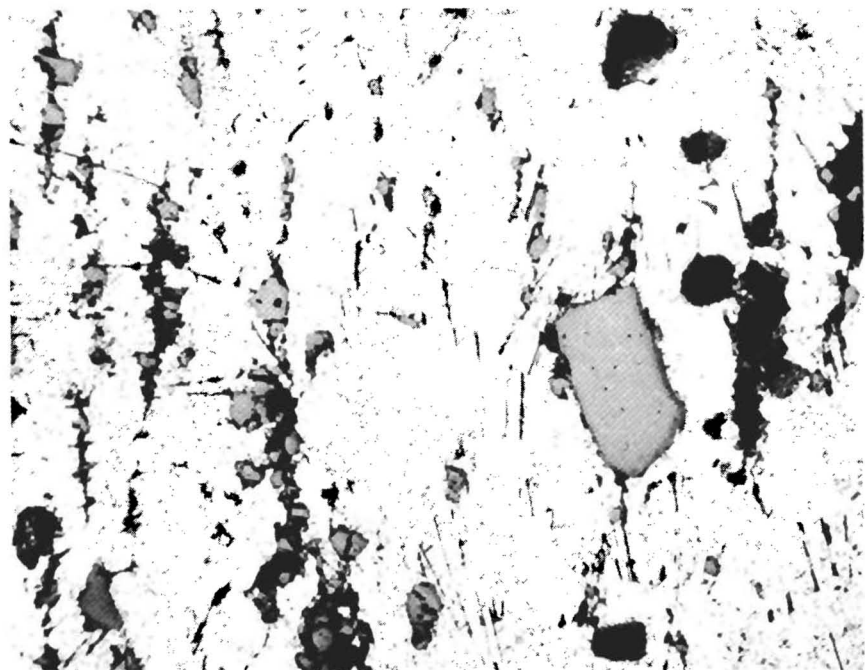


Figure 11. Line of Demarcation of Exuded Metal Region in 1380° F Sag Test, Etched in 0.5% HF (62x).



a. Unetched



b. Etched in 0.5% HF

Figure 12. Original Sample Region after 1380° F Sag Test (250x)

led



Figure 14. ATR Dispersion Sag Tested by  $1710^{\circ}$  F (7x).

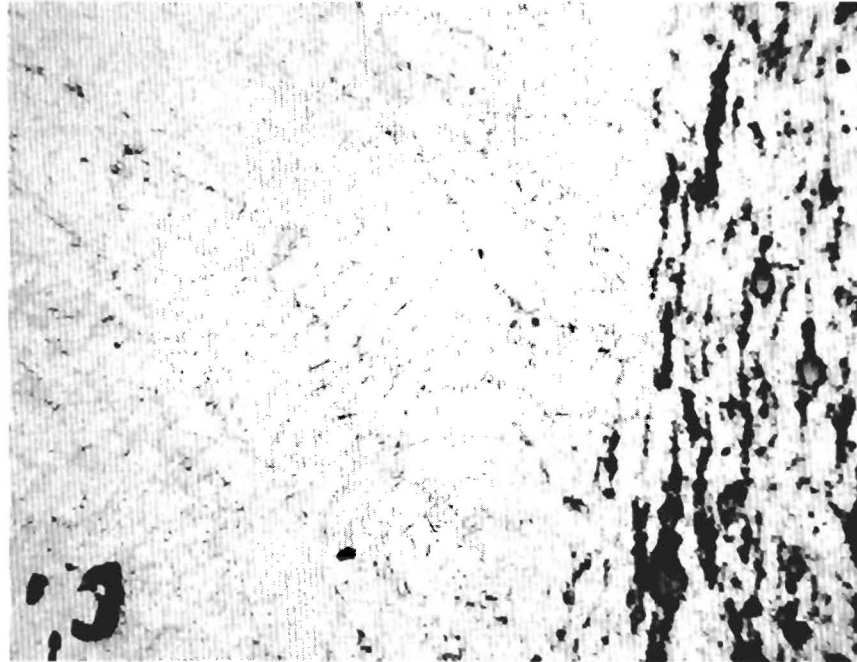
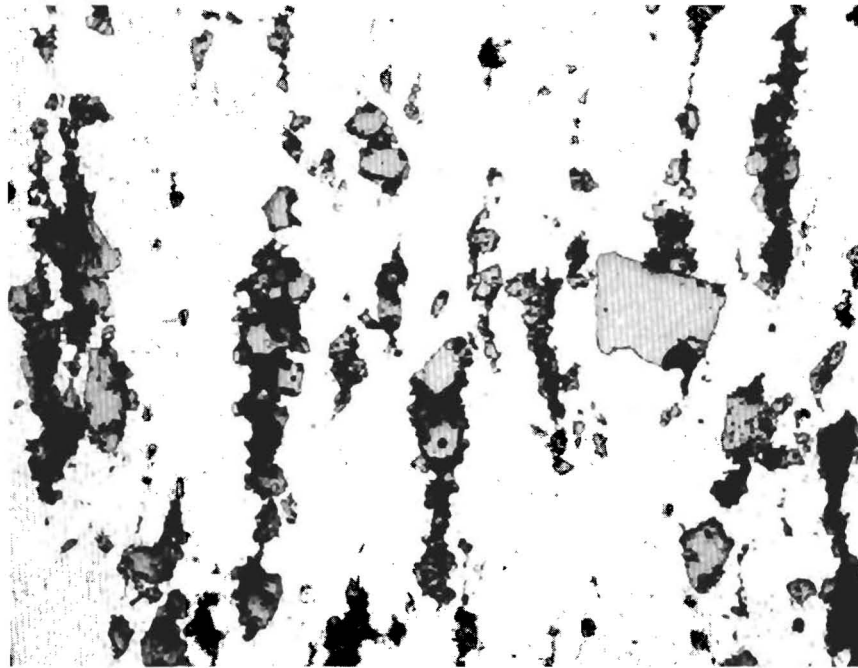
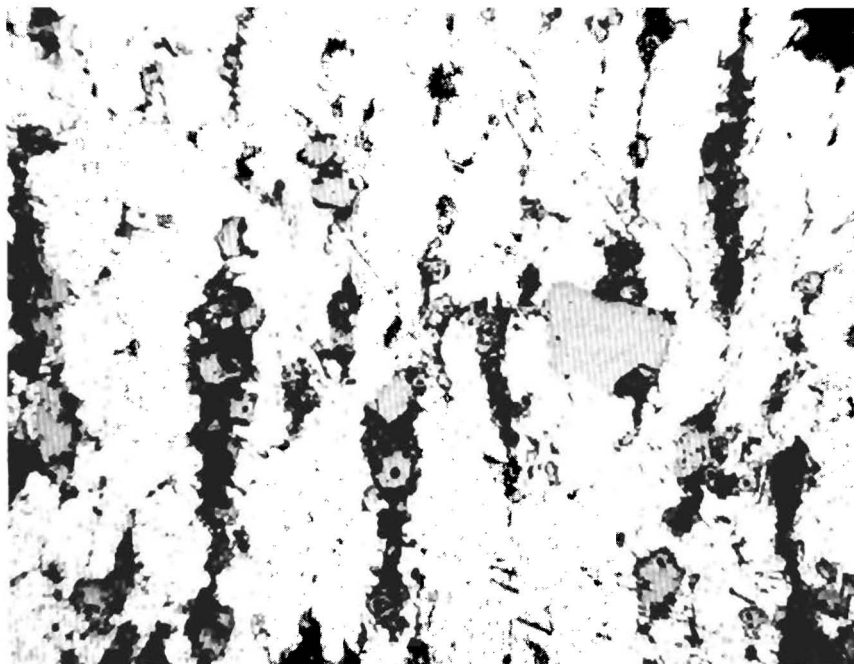


Figure 15. Line of Demarcation of Exuded Metal Region in 1710<sup>o</sup> F Sag Test, Etched in 0.5% HF (62x).

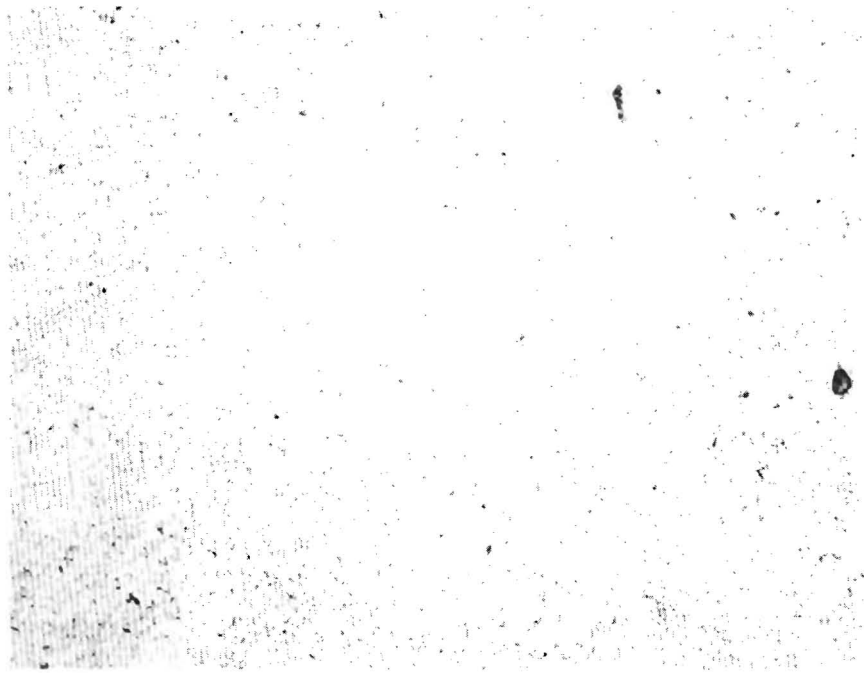


a. Unetched

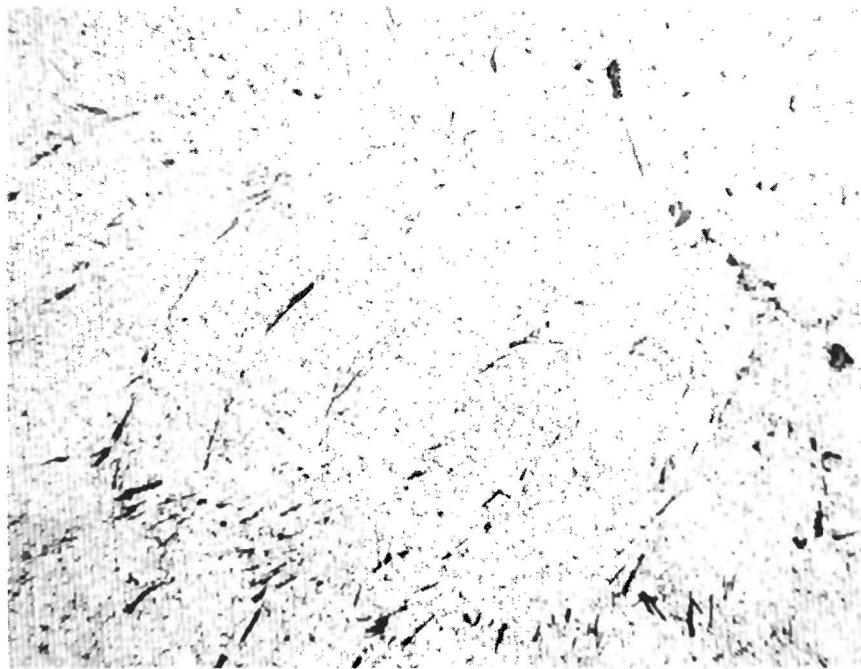


b. Etched in 0.5% HF

Figure 16. Original Sample Region after 1710<sup>o</sup> F Sag Test (250x).



a. Unetched



b. Etched in 0.5% HF

Figure 17. Exuded Metal Region in 1710<sup>o</sup> F Sag Test (250x).

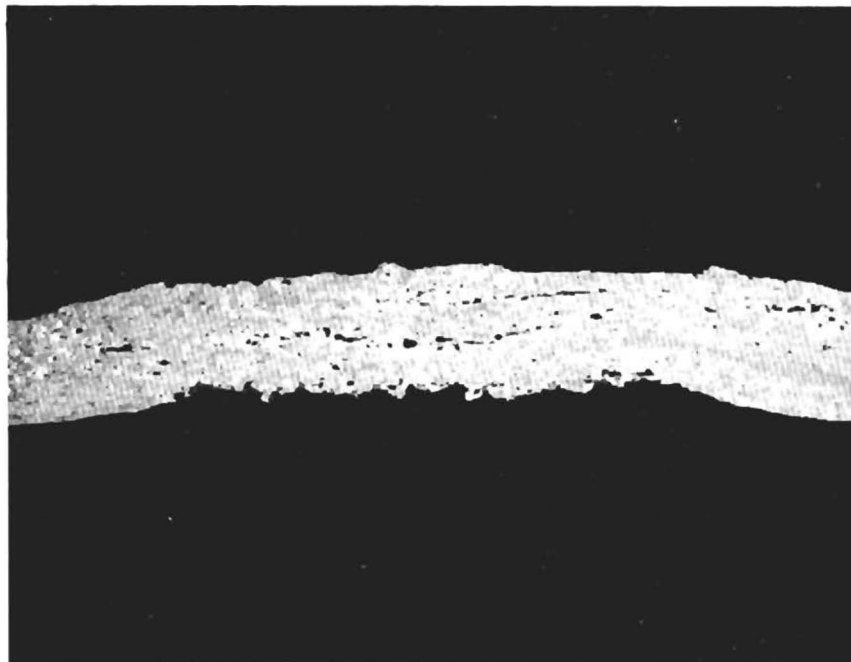


Figure 18. ATR Dispersion Sag Tested at  $1860^{\circ}$  F (7x).

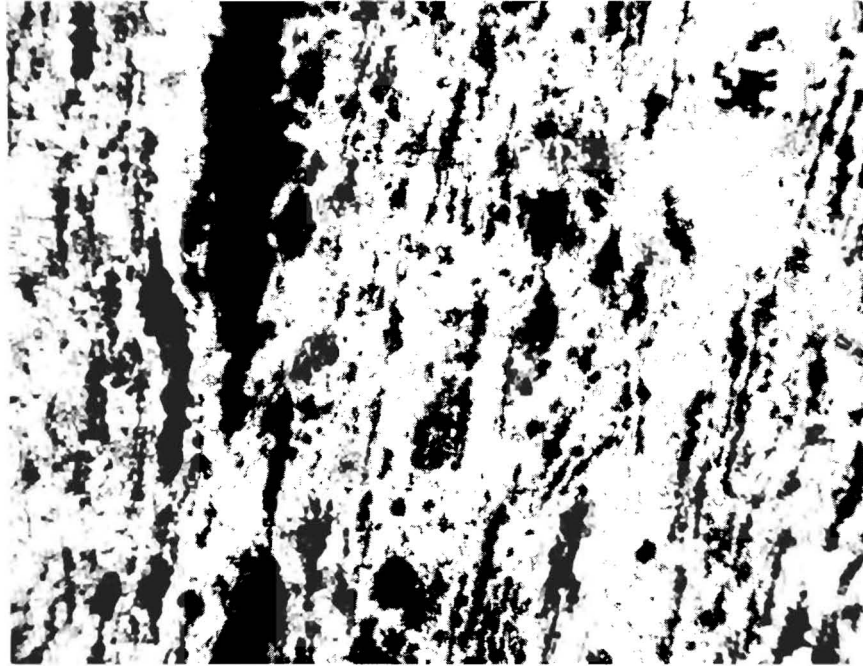
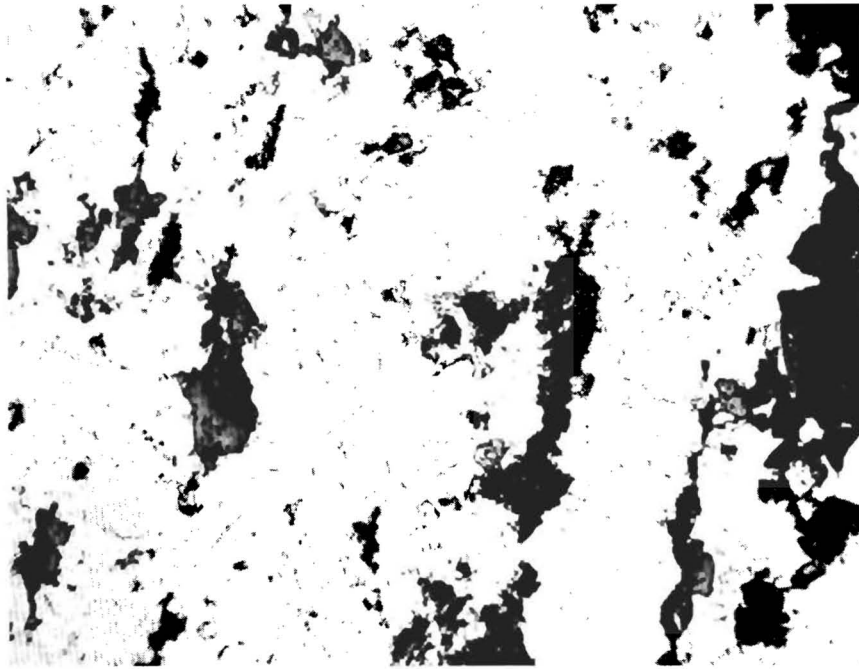
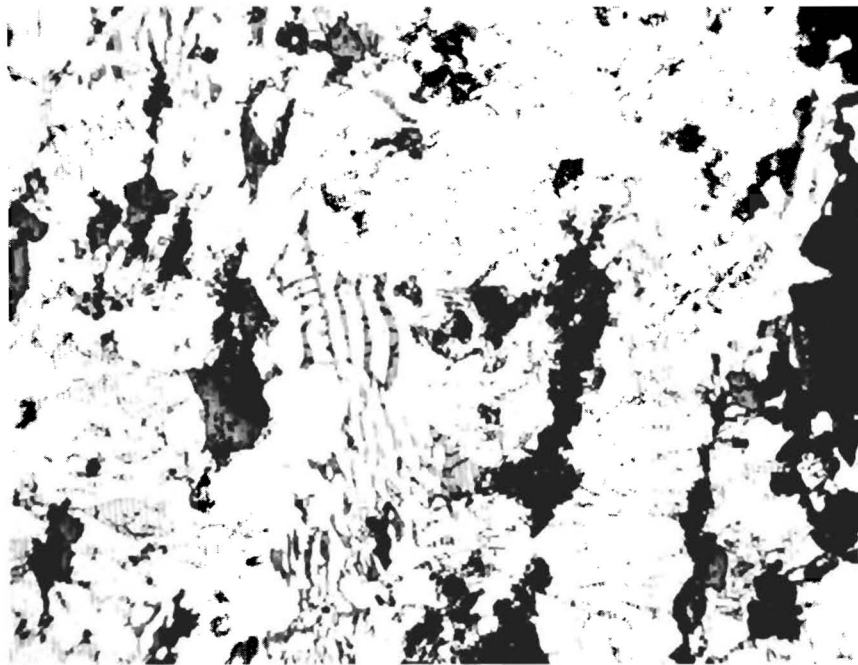


Figure 19. ATR Dispersion Sag Tested at 1860<sup>o</sup> F, Etched in 0.5% HF (62x).





a. Unetched



b. Etched in 0.5% HF

Figure 20. ATR Dispersion Sag Tested at 1860° F (250x).

where  $C_{U_3O_8}$  represents the conversion of  $U_3O_8$  to uranium and  $x_U$  represents the weight fraction of uranium in the resulting alloy assuming homogeneity. This shows that 33.2 per cent of the  $U_3O_8$  would have to be reduced in order to yield an alloy of greater uranium content than the Al- $UAl_4$  eutectic at 13 per cent uranium. Comparison of Figures 9 and 12 is sufficient to indicate that far less than 33 per cent of the original  $U_3O_8$  was reduced in the 1380° F specimen. More reduction, approximately 48.1 per cent, would be required to put the 1380° F specimen in any field containing  $UAl_3$  even if the temperature measurement were in error. As a result, a safe conclusion is that only  $UAl_4$  could form in the 1380° F specimen. If this were not sufficient proof, a further indication is given by the appearance of the blue-staining phase in the exuded metal region. If  $UAl_3$  had formed within the specimen during testing, it probably would have remained in the original sample area since movement of solid particles through the oxide network would be very restricted. The only apparent way that the blue-staining phase could appear in the exudate is for the exuded material to have been a molten U-Al solution from which the particles precipitated on cooling. Such a precipitation would necessarily be  $UAl_4$ .

As previously noted, the exudate in both of the lower temperature specimens, Figure 13 and 17, is remarkably free of uranium oxides. This provides additional support for the suggestion that the oxides are held in place by a refractory network, probably of  $Al_2O_3$ .

The explanation for the much higher strength of the 1860° F specimen is fairly clearly indicated by the microstructure, Figure 20. Almost all of the  $U_3O_8$  is seen to have been reduced, implying the existence of a more

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extensive  $\text{Al}_2\text{O}_3$  substructure. The reaction was apparently complete enough to bring the sample through a  $\text{UAl}_3$  phase region since a greater bulk of light-staining  $\text{UAl}_3$  (?) than of dark-staining  $\text{UAl}_4$  (?) is obvious. This  $\text{UAl}_3$  (?) was retained by the fast cooling given the sample after completion of the test. The  $\text{UAl}_3$  (?) could not have contributed to the strength at the testing temperature since the metal phase would almost certainly have been molten during the sag test.

Further evaluations of the sag tests will be made after the effects of the HF etchant are more completely determined.

IV. 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. Paul Boland	Group Leader
Mr. S. H. Bomar	Group Leader
Mr. N. K. Hearn	Assistant Research Physicist
Mr. M. L. Calhoun	Technician
Mr. P. A. Darius	Technician
Mr. A. C. Evans	Technician
Mr. G. W. Smith	Technician

Submitted by:

*for* J. D. Fleming  
Senior Investigator

J. W. Johnson  
Assistant Project Director

Approved:

J. D. Walton, Head  
High Temperature Materials Branch

F. Bellinger, Chief  
Chemical Sciences and Materials Division

V. APPENDIX

STATISTICAL SUMMARY FOR HIGH TEMPERATURE TENSILE TESTS

STATISTICAL SUMMARY FOR HIGH TEMPERATURE TENSILE TESTS

<u>Firing Temperature</u> (°F)	<u>Firing Time</u> (hr)	<u>Testing Temperature</u> (°F)	<u>Variance Estimate (<math>S^2</math>)</u> (psi <sup>2</sup> )	<u>95% Confidence Interval</u> (psi)	<u>Coefficient of Variation</u> (%)
1800 (Bisque)	2	Ambient	4,827	510 $\pm$ 50	14
2133	19	Ambient	402,907	3210 $\pm$ 450	20
		400	631,071	3780 $\pm$ 570	21
		800	912,804	4790 $\pm$ 680	20
		1200	1,007,957	5860 $\pm$ 720	17
		1600	1,069,032	6960 $\pm$ 740	15
		2000	6,107,427	8650 $\pm$ 1770	29
2166	8.5	Ambient	306,032	2620 $\pm$ 400	21
		400	285,796	3410 $\pm$ 380	16
		800	391,160	5260 $\pm$ 450	12
		1200	1,375,068	5770 $\pm$ 840	20
		1600	1,281,823	6550 $\pm$ 810	17
		2000	3,759,432	8180 $\pm$ 1390	24

(Continued)

STATISTICAL SUMMARY FOR HIGH TEMPERATURE TENSILE TESTS (Continued)

<u>Firing Temperature</u> (°F)	<u>Firing Time</u> (hr)	<u>Testing Temperature</u> (°F)	<u>Variance Estimate (<math>S^2</math>)</u> (psi <sup>2</sup> )	<u>95% Confidence Interval</u> (psi)	<u>Coefficient of Variation</u> (%)
2200	0.5	Ambient	93,512	2260 $\pm$ 220	14
		400	248,267	2600 $\pm$ 360	19
		800	235,010	2680 $\pm$ 350	18
		1200	103,586	2700 $\pm$ 250	12
		1600	285,533	2960 $\pm$ 380	18
		2000	569,188	3690 $\pm$ 540	20
2200	2	Ambient	190,444	4300 $\pm$ 310	10
		400	1,191,661	4270 $\pm$ 840	26
		800	1,170,912	5000 $\pm$ 770	22
		1200	1,064,712	4680 $\pm$ 740	22
		1600	1,760,382	5930 $\pm$ 950	22
		2000	3,300,477	7510 $\pm$ 1300	24

(Continued)

STATISTICAL SUMMARY FOR HIGH TEMPERATURE TENSILE TESTS (Continued)

<u>Firing Temperature</u> (°F)	<u>Firing Time</u> (hr)	<u>Testing Temperature</u> (°F)	<u>Variance Estimate (<math>S^2</math>)</u> (psi <sup>2</sup> )	<u>95% Confidence Interval</u> (psi)	<u>Coefficient of Variation</u> (%)
2200	3.3	Ambient	867,130	3430 ± 670	27
		400	639,046	4550 ± 570	18
		800	561,921	5040 ± 540	15
		1200	1,577,579	5940 ± 720	21
		1600	1,974,232	5970 ± 1010	24
		2000	4,423,027	7980 ± 1500	26
2200	5	Ambient	377,139	2550 ± 440	24
		400	400,810	3270 ± 450	19
		800	560,632	4720 ± 540	16
		1200	793,517	5390 ± 640	17
		1600	2,593,284	5650 ± 1150	29
		2000	8,802,173	7010 ± 2120	42

(Continued)



STATISTICAL SUMMARY FOR HIGH TEMPERATURE TENSILE TESTS (Concluded)

<u>Firing Temperature</u> (°F)	<u>Firing Time</u> (hr)	<u>Testing Temperature</u> (°F)	<u>Variance Estimate (<math>s^2</math>)</u> (psi <sup>2</sup> )	<u>95% Confidence Interval</u> (psi)	<u>Coefficient of Variation</u> (%)
2200	8	Ambient	20,783	1700 $\pm$ 100	9
		400	15,539	1830 $\pm$ 90	7
		800	69,404	3350 $\pm$ 190	8
		1200	314,636	4120 $\pm$ 430	14
		1600	262,595	3990 $\pm$ 470	13
		2000	3,343,250	4370 $\pm$ 1530	42

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VI. PRIOR REPORTS

Previous reports issued under this contract are:

1. Monthly Letter Reports Nos. 1 - 57, Issued each month since December 1958.
2. Progress Report No. 1, August 1959. Issued as ORO-209 by OTS, Department of Commerce.
3. Progress Report No. 2, Part 1, August 1960, Issued as ORO-325 by OTS, Department of Commerce.
4. Progress Report No. 2, Part 2 (Declassified), August 1960.
5. Progress Report No. 3, August 1961.
6. Quarterly Report No. 1, April 1962.
7. Summary Report No. 1, July 1962.
8. Quarterly Report No. 2, October 1962.
9. Quarterly Report No. 3, January 1963.
10. Quarterly Report No. 4, April 1963.
11. Summary Report No. 2, June 1963.

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QUARTERLY REPORT NO. 6

PROJECT NO. B-153

MATERIALS FOR HIGH TEMPERATURE  
NUCLEAR ENGINEERING APPLICATIONS

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

Paul Boland, and S. H. Bomar

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

Contract No. AT-(40-1)-2483

1 January

Engineering Experiment Station  
**GEORGIA INSTITUTE OF TECHNOLOGY**  
Atlanta, Georgia



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

QUARTERLY REPORT NO. 6

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Oak Ridge Operations Office  
Oak Ridge, Tennessee

October 1, 1963 to January 1, 1964

Quarterly Report No. 6, Project No. B-153

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Quarterly Report No. 6, Project No. B-153

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 October 1, 1963 to January 1, 1964.

## I. INTRODUCTION

During recent years, fused silica has assumed the status of an engineering material. With the development of slip-casting techniques, the fabrication cost has been decreased substantially and much more complex shapes are feasible. Slip-cast fused silica is currently being used in many critical applications ranging from brazing and heat treating fixtures for supersonic aircraft components to prototype radomes for hypersonic missiles. The properties which have made slip-cast fused silica suitable for these uses combine with good radiation resistance to recommend it for use in high temperature nuclear applications. One object of Project B-153 is the development and compilation of data sufficient to evaluate slip-cast fused silica for such nuclear applications.

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  $U_3O_8$ . Since Al- $U_3O_8$  dispersions are in common use as reactor fuels, the results of this study are obviously of interest in hazards evaluation. Several special studies of Al- $U_3O_8$  dispersions are included in the program to assist hazards evaluation.

## II. SUMMARY

Brief determinations were made of the physical properties of two types of foam prepared from fused silica slip. Nominal 25 lb<sub>m</sub>/ft<sup>3</sup> foam displayed a compressive strength of approximately 400 psi at room temperature and 540 psi at 2000° F. Nominal 50 lb<sub>m</sub>/ft<sup>3</sup> foam showed compressive strengths of approximately 1250 and 1050 psi at room temperature and 2000° F respectively. The cristobalite content was less than 2 per cent in each foam.

Efforts to measure reaction kinetics in Al-U<sub>3</sub>O<sub>8</sub> dispersions were continued. A new dispersion of ATR composition was found to undergo catastrophic swelling at elevated temperatures, causing loss of beam alignment in the dynamic x-ray system. This dispersion was replaced with a reference plate from the ORNL development study of ATR plates. X-ray specimens were cut from this plate and the cladding was machined from one side to expose the fuel meat. Supporting the sample on the remaining clad side was not successful. At testing temperatures, the cladding flowed significantly although the fuel meat did not. This again caused loss of x-ray beam alignment. The problem was solved by inverting the x-ray furnace, supporting the specimen on the fuel meat side upon a stainless steel grid, and carrying out diffraction from below the horizontal axis of the goniometer. Kinetics runs were begun using the modified arrangement.

A new replication technique was developed which permits location of specific areas in ATR dispersions for electron micrography. The technique consists of producing a polyvinyl alcohol replica from which a secondary nitrocellulose replica is formed and stripped. The nitrocellulose replica is shadowed with platinum and coated with carbon. After dissolution of the

nitrocellulose in amyl acetate or acetone, the carbon-platinum replica is left intact instead of fragmented as is usually the case. The replica can be indexed with the sample and areas observed optically on the sample or the polyvinyl alcohol replica can be located quickly on the carbon-platinum replica in the electron microscope. The polyvinyl alcohol replica is not destroyed in the process and can be used to produce a series of carbon-platinum replicas if desired.

### III. EXPERIMENTAL PROGRESS AND DISCUSSION

#### A. Foamed Fused Silica

In order to supplement the data available for various forms of fused silica, brief tests were made on two types of open pore foam formed from fused silica slip. Samples of No. 25 and No. 50 foam were obtained from Glasrock Products, Inc.<sup>1/</sup> Two types of specimens were prepared from each sample, a 1 x 1-1/2 x 6-inch modulus of rupture specimen and a 3/4-inch diameter cylinder 2-inches long for porosity and compressive strength determinations.

Modulus of rupture in three point loading and room temperature compression tests were made on a Tinius-Olsen Super L universal tester. Compression tests were made at 2000° F in the ring tensile tester. Bulk density, porosity, and apparent theoretical density measurements were made by air displacement. The cristobalite contents of the foams were determined by powder x-ray diffraction.

Twenty replicates were used in the modulus of rupture and air displacement tests, ten in the compressive strength determinations, and a single representative powder blend in the x-ray tests.

The results of these studies are given in Table I.

---

<sup>1/</sup>Glasrock Products, Inc., 1101 Glidden St., Atlanta, Georgia.

TABLE I  
PROPERTIES OF FUSED SILICA FOAM<sup>1/</sup>

Property	No. 25 <sup>2/</sup>	No. 50 <sup>2/</sup>
Bulk Density ( $\frac{\text{gm}}{\text{cc}}$ )	0.459 $\pm$ 0.004	0.760 $\pm$ 0.003
Porosity (%)	79.55 $\pm$ 0.33	66.58 $\pm$ 0.35
Apparent Theoretical Density ( $\frac{\text{gm}}{\text{cc}}$ )	2.253 $\pm$ 0.041	2.276 $\pm$ 0.017
Modulus of Rupture	121 $\pm$ 6	409 $\pm$ 20
Compressive Strength		
Room Temperature	399 $\pm$ 25	1252 $\pm$ 77
2000° F	540 $\pm$ 127	1050 $\pm$ 183
Cristobalite Content (%) (Referred to A-4 Standard)	1.4	1.8

<sup>1/</sup>Ranges shown are for the 95 per cent level of confidence in the mean.

<sup>2/</sup>No. 25 is nominally 25 lb<sub>m</sub>/ft<sup>3</sup> foam. No. 50 is nominally 50 lb<sub>m</sub>/ft<sup>3</sup>.

Since the values in Table I were obtained from a single batch of each of the foams, they must be regarded as only typical. No indication of the run-to-run variation in properties can be implied.

The variation in properties within the batch is quite low as is shown by the various ranges of the different parameters. The only significant variation observed was in the 2000° F compressive strength. This variation must be assigned in part to the adaption of the ring tester to compression testing. The same factor must be kept in mind when comparing the low and high temperature compressive strengths which showed a statistically significant increase in strength with temperature for No. 25 foam and statistically significant decrease for No. 50 foam.

## B. Al-U<sub>3</sub>O<sub>8</sub> Interactions

### 1. Determination of Reaction Kinetics

Since the initial ATR composite was completely expended in earlier work, a new dispersion of similar composition was obtained from ORNL for the dynamic x-ray tests. Samples cut from these plates 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 the first in microstructure or composition except that spectrographic analysis showed no nickel. A detailed review of handling techniques by ORNL and Georgia Tech personnel failed to indicate any sources of difference in the production

of the new dispersion or in the preparation of the x-ray specimens.

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 the first dispersion did not swell unduely in the x-ray tests, 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 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<sub>3</sub>O<sub>8</sub> fuel meat. High temperature x-ray runs were begun to determine the Al-U<sub>3</sub>O<sub>8</sub> reaction rate. 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.

In preliminary tests, the inverted x-ray system performed well with the reference fuel plate specimens and kinetics runs were begun.

## 2. Replication for Electron Micrography

Attempts were made to develop methods for relocating areas on the  $\text{Al-U}_3\text{O}_8$  dispersions for repeated replication and for comparison with optical micrographs. Location was occasionally possible with the conventional PVA (polyvinyl alcohol) process but usually the carbon replica shattered during dissolution of the PVA.

The conventional PVA replication process was modified by the addition of an intermediate step. Following removal of the PVA, it was replicated with a nitrocellulose solution 1/. The secondary replica was then stripped from the PVA primary replica, platinum shadowed, and carbon coated. Floating in amyl acetate or acetone removed the secondary nitrocellulose, leaving behind the intact carbon-platinum replica which was picked up and handled in the usual manner.

Replication by this process permits location of specified areas by indexing the carbon and PVA replicas under a stereo microscope or by means

---

1/Either U. S. Industrial Chemical Company J26A or collodion.

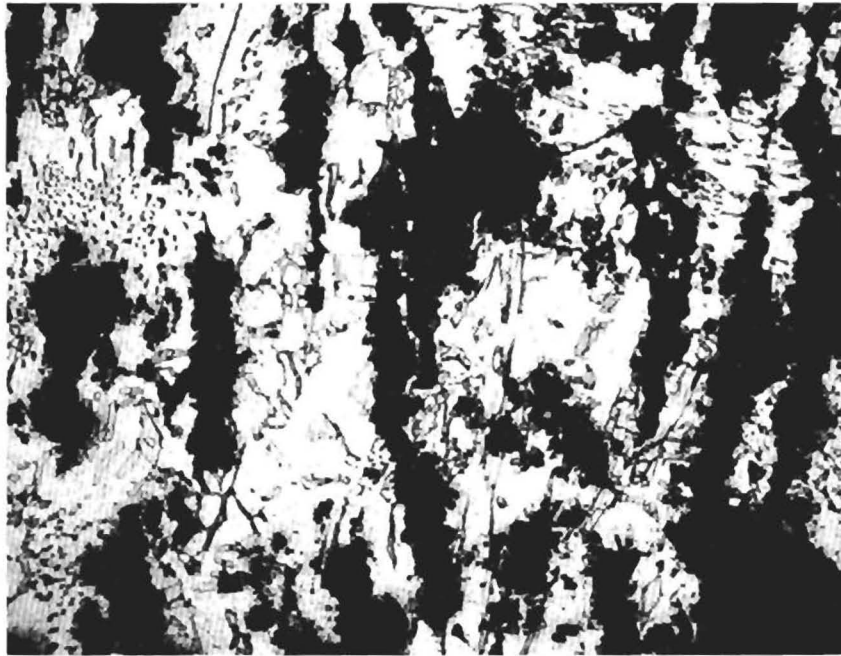
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of index indentations on the sample. Once the indexing is accomplished, the selected area can be located in the electron microscope by using an optical microscope to determine the co-ordinates of the desired area on either the sample or the PVA replica relative to the index, and setting the same co-ordinates on the electron microscope stage controls. This is sufficiently accurate to locate the area at low power and specific features can then be examined at the high power as usual.

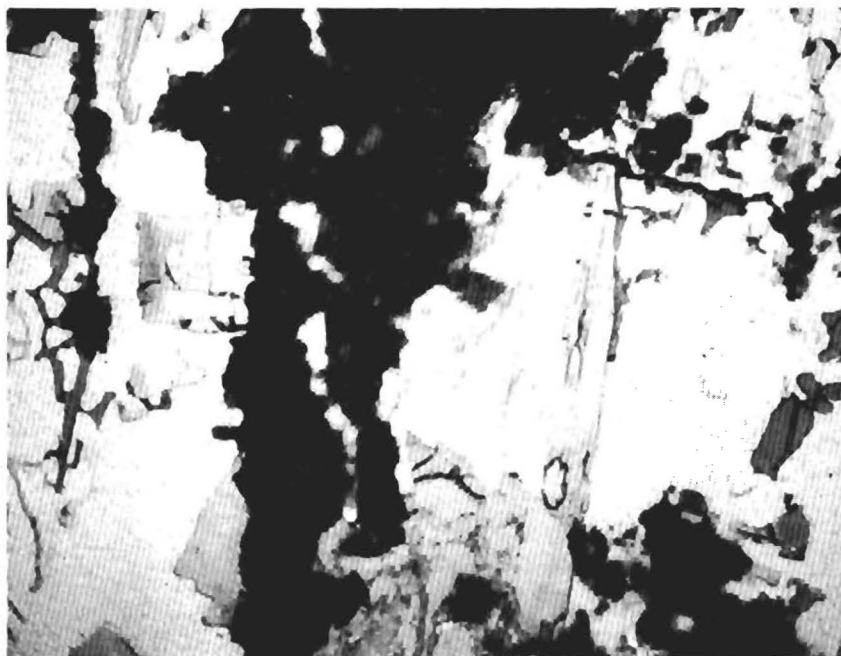
The new process also retains the PVA master replica, so that as many carbon replicas can be produced from the same area as are desired.

An example of this type of replication is shown in Figures 1 and 2. An electron micrograph was to be made of the square particle seen in Figure 1. The new process was carried out as above and the area was quickly located by means of the index point on the intact carbon replica. The square  $UAl_3$  particle is shown in Figure 2. The electron micrograph shows clearly the rim of  $UAl_4$  around the periphery of the particle.

As time permits, the new replication process will be applied to studies of the reaction mechanisms in serial-heated  $Al-U_3O_8$  dispersions.



a. 250x



b. 575x

Figure 1. Optical Micrograph of Al-U<sub>3</sub>O<sub>8</sub> Dispersion Etched in 0.5% HF.

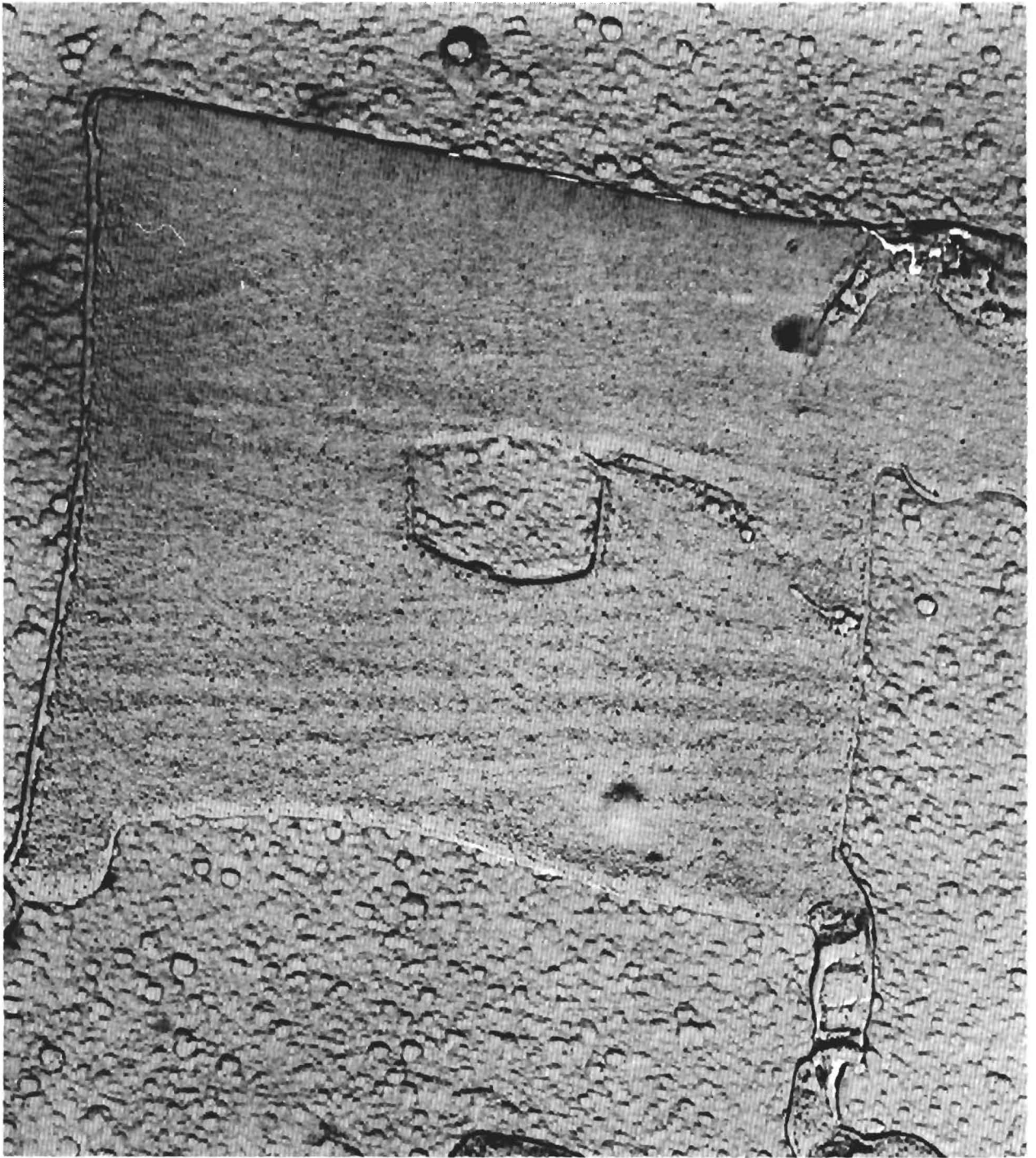


Figure 2. Electron Micrograph of Al- $\text{U}_3\text{O}_8$  Dispersion Etched in 0.5% HF (8000x).

IV. 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:

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Mr. S. H. Bomar	Group Leader
Mr. P. A. Darius	Technician
Mr. A. C. Evans	Technician
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V. PRIOR REPORTS

Previous reports issued under this contract are:

1. Monthly Letter Report Nos. 1 - 60, Issued each month since December 1958.
2. Progress Report No. 1, ORO-209, August 1959.
3. Progress Report No. 2, ORO-325, Part 1, August 1960.
4. Progress Report No. 2, ORO-325, Part 2 (Declassified), August 1960.
5. Progress Report No. 3, ORO-577, August 1961.
6. Quarterly Report No. 1, ORO-578, April 1962.
7. Summary Report No. 1, TID-17322, July 1962.
8. Quarterly Report No. 2, TID-17530, October 1962.
9. Quarterly Report No. 3, TID-18286, January 1963.
10. Quarterly Report No. 4, TID-18891, April 1963.
11. Summary Report No. 2, TID-19057, June 1963.
12. Quarterly Report No. 5, October 1963.

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