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EFFECT OF TITANIUM DIOXIDE AS A MINERALIZER
IN SILICA BRICK

BY

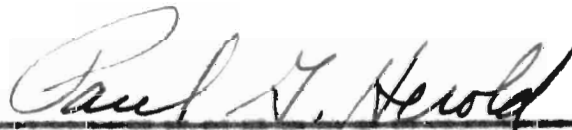
HENRY CLAY BRASSFIELD

A

THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree of
MASTER OF SCIENCE, CERAMIC ENGINEERING
Rolla, Missouri
1949

Approved by



Dr. Paul G. Herold, Chairman, Department of
Ceramic Engineering

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INTRODUCTION

The magnitude of the thermal expansion of silica brick and its inability to withstand rapid temperature changes gives rise to problems of considerable importance in the manufacture of silica brick.

In firing the silica brick, mineralogical changes occur in the quartzite from which the brick is made, in which minerals of lower specific gravity are formed. This results in a permanent expansion of the brick. These mineralogical changes have been thoroughly studied and considerable information is known on the different forms of silica produced at the higher temperatures. If the conditions of firing are such that these changes have progressed but little during the initial firing of the brick it is quite certain that if the brick are used in service where they are subjected to a high temperature, further permanent expansion will occur. This expansion results, generally, in buckling and cracking of the silica brick walls.

The changes causing this expansion are due to the quartz changing over into tridymite and cristobalite and due to the unconverted quartz changing from alpha to beta quartz. From the thermal expansion data for the different forms of silica, it is seen that tridymite has the most desirable thermal expansions characteristics for

silica refractories, and for this reason it is desired to convert as much of the silica possible to the tridymite form in the initial firing of the silica brick. Tridymite has the most desirable thermal expansion characteristics and for this reason it is desired to convert as much of the quartz as possible to the tridymite form in the initial firing of the silica brick. However, the change from the beta form of quartz over to either the tridymite or cristobalite form is very slow and the change from quartz to tridymite does not occur in the absence of a flux. This sluggish inversion or change necessitates the long firing period used in the manufacture of silica brick.

If some satisfactory substance could be found which would act as a mineralizer or catalyst in the reaction the burning time could be shortened and a considerable saving in fuel costs realized.

Titanium dioxide is a frequent impurity in the quartzite and is present in amounts of a trace up to one percent or more. Several investigators have studied the effect of titanium dioxide on silica brick but have presented no conclusive evidence as to whether it acted in any beneficial way in the formation of either cristobalite or tridymite. However, it was found that brick containing titanium dioxide have greater resistance to thermal shock and spalling. These studies were all made using the pet-

rographic microscope method of analysis to obtain the end result. No satisfactory explanation was given for the increased resistance to spalling and thermal shock.

In view of these findings it was decided to study the effect of additions of titanium dioxide by means of quantitative analysis by x-ray methods, and by this meth-^{od} of arrive at more definite conclusions as to the effect of titanium dioxide on the silica brick. It was hoped that the reactions could be studied at the actual firing temperatures used in silica brick manufacture.

REVIEW OF LITERATURE

(1)

The work of Fenner provides a very complete summation of the work done on the transformation or inversion points of quartz. The inversions and temperatures of the inversion points as determined by Fenner are as follows:

575°C alpha quartz beta quartz; 570° beta quartz to alpha quartz.

870°C 10° beta quartz tridymite

1470°C 10° tridymite cristobalite

117°C alpha tridymite beta₁ tridymite; 165°

beta₁ tridymite to beta₂ tridymite, reversions on cooling are not sharp.

274.6 - 219.7° C alpha cristobalite beta cristobalite.

240.5 - 198.1° C beta cristobalite alpha cristobalite.

At ordinary temperatures each mineral exists only in the alpha phase and all change into the beta form as the temperature is raised. The change from the alpha to the beta forms is rapid but the change from the beta form of one mineral to another requires considerable time except at extremely high temperatures.

(1) Fenner, C. N., The stability relations of the silica minerals. Am. Jour. of Sci., Series 4, Vol. 36, p. 383, 1913.

(2) Ibid. p. 358.

In the presence of a flux, when any form of quartz is heated for a sufficiently long time below 870°C , quartz is always formed. Between 870°C and 1470°C tridymite and from 1470°C up to the melting point of silica, cristobalite. However, if heated without a flux the inversion from quartz to tridymite does not occur but the transformation is direct to cristobalite. In many cases the transformation is direct to cristobalite. In many cases the transformation follows Ostwald's rule; that is, an unstable form does not pass directly into the most stable form, but the action progresses through successive steps and intermediate phases appear, which eventually reach the stage of greatest stability.

The velocity of these transformations are very slow. (3)
 McDowell, (4) from experimental evidence obtained by the repeated firing of bricks made from Medina quartzite considers that it would require 16 or 17 firings to convert the whole of the quartz into tridymite.

Various oxides and other substances have been suggested from time to time as catalysts for increasing the rate of the quartz inversion. Fenner (5) has reported heating

(3) Ibid. p. 334.

(4) McDowell, J. S., A study of silica refractories. Am. Inst. of Mining Engineers Bull., Nov. 1916.

(5) Fenner, op. cit. p. 336.

quartz with sodium tungstate and getting complete inversion to cristobalite and tridymite, and the form obtained depending on the temperature and duration of the heat treatment. The amount of sodium tungstate was considerably in excess of the amount of lime bond ordinarily used in silica brick manufacture.

(6)
Hugill and Rees added iron oxide in amounts of 2% to a standard silica brick batch and results showed a ground mass of interlocking tridymite crystals and only the largest quartz grains are unchanged. Bricks made with iron oxide were also tested in an acid open hearth furnace (7) and gave results superior to the straight lime bonded bricks.

(8)
Hugill and Rees also studied the effect of titanium dioxide in silica brick with regard to the influence on the rate of inversion of the quartz to tridymite and cristobalite. Titanium dioxide was added in increments of one percent up to two percent. Results were studied with the petrographic microscope and the conclusion drawn that the titanium dioxide had no appreciable effect on

(6) Hugill, W. and Rees, W. J., The Influence of Iron Borate on the Rate of Quartz Inversion in Lime and Clay Bonded Silica Brick, Trans. Cer. Soc. (Eng.) 30, p. 321, 1930-31.

(7) Ibid. p. 333.

(8) Hugill, W. and Rees, W. J., The Influence of Titanium Dioxide on the Rate of Quartz Inversion in Lime Bonded Silica Brick. Trans. Cer. Soc. (Eng.) 30, p. 347, 1930-31.

the rate of inversion. It was noted that there was a slightly greater percent of tridymite in the ground mass of the brick and that the bricks containing the titanium dioxide had greater resistance to thermal shock and spalling. This was attributed to the felted structure of the ground mass which allowed greater movement to take place without rupture.

The effect of 2% addition of iron borate to a lime bonded silica brick was studied by Hugill and Rees⁽⁹⁾ and it was determined that the presence of boric oxide had little effect on the rate of inversion and that it was the iron oxide which increased the rate of inversion.

Lynam and Rees⁽¹⁰⁾ studied the effect of oxides of iron and chromium in a reducing atmosphere. The microstructure of the bricks show decidedly less tridymite in the bricks burned under completely reducing conditions. They state further that the bricks burned in the reducing atmosphere were enclosed in saggars and became permeated with fine carbon. The fine carbon may have prevented spreading of the iron compounds and tended to prevent close contact of the melt with the quartz grains.

(9) Hugill, W. and Rees, W. J., The Influence of Iron Borate on the Rate of Inversion of Quartz in Silica Brick, Trans. Cer. Soc. (Eng.) 29, p. 299, 1930.

(10) Lynam, F. R. and Rees, W. J., The Effect of Oxides of Iron and Chromium and a Reducing Atmosphere on the Rate of Tridymite Formation in a Silica Brick, Trans. Cer. Soc. (Eng.) 34, p. 507, 1934-35.

Several catalysts were studied by Taylor and Lin⁽¹¹⁾ over temperature ranges from 1000°C to 1450°C. The results were compared by determining the true specific gravity of each mix and comparing the effect of the different catalysts in this manner. The list of substances tried are too numerous to list here.

The literature survey dealing with the effect of added substances on the inversion rate of quartz yielded many more references. However it is difficult to compare the end result as the analysis of the material used is not given and some of the impurities may have masked or disturbed the effect of the added constituent. Also there are many contradictions between the results reported.

(11) Taylor, N. W. and Lin, Cho-Yuan, Effect of Various Catalysts on Conversion of Quartz to Cristobalite and Tridymite at High Temperatures, Jour. Am. Cer. Soc. 24, pp. 57-63, 1941.

QUANTITATIVE ANALYSIS BY X-RAY METHODS

Before discussing the experimental procedure and the results obtained, it would be of advantage to briefly discuss the method of quantitative analysis by x-ray diffraction and some of the precautions to be taken to obtain accurate results.

The x-ray equipment used in this study was the Morelco X-ray Diffraction Spectrometer made by the North American Phillips Company. CuK_α radiation was used throughout the work. With this spectrometer the conventional film is replaced by a Geiger counter tube, the output of which is amplified and fed to a strip chart recorder or an impulse counter. In this way a plot of intensity of the various diffractions vs. angle is obtained. Theoretically, the intensity of the diffraction line is directly proportional to the amount of the particular constituent in the sample being analysed. This assumes that the absorption and particle size of all constituents in the sample are the same.

The speed of scanning of the sample may be varied from 0.25° to 4° θ per minute by using the drive motors available for the scanning arm.

Since this machine became available considerable interest has been shown in developing methods which could be used for accurate quantitative analysis. Of particu-

lar interest in this study is the work of Alexander, Klug and Kummer.⁽¹²⁾ A study was made of the statistical factors affecting the intensity of the x-rays diffracted by crystalline powders. Table I shows the effect of particle size on the reproducibility of results when the substance analyzed is quartz. The relationship between particle size and reproducibility of results is well illustrated.

Alexander and Klug⁽¹³⁾ also studied the effect of absorption of different constituents in the sample to be analyzed. The intensity of mixtures of quartz and cristobalite was measured and found to be a straight line function and in all such cases where the absorption is the same the intensity is directly proportional to the amount of the constituent in the sample if the particle size is equal.

For samples containing constituents of widely different absorption power the internal standard method must be used to obtain the working curve from which the percentage of unknown can be found. In this method a known amount of the unknown to be tested for in the sample is added to a

-
- (12) Alexander, L., Klug, H. P. and Kummer, E., Statistical Factors Affecting the Intensity of X-rays Diffracted by Crystalline Powders. *Jour. Applied Physics*, 19, pp. 742-53, 1948.
- (13) Alexander, L. and Klug, H. P., Basic Aspects of X-ray Absorption in Quantitative Diffraction Analysis of Powder Mixtures. *Anal. Chem.* 20, pp. 886-89, 1948.

TABLE I

Intensity measurements on fractions of 325 mesh quartz powder. Tabulated values are areas in arbitrary units of the 3.33\AA^0 maximum as counted with the Geiger-counter x-ray spectrometer using CuK_α radiation.

Specimen No.	15-50 micron fraction	5-50 micron fraction	5-15 micron fraction	-5 micron fraction
1	7,612	8,688	10,841	11,055
2	8,373	9,040	11,336	11,040
3	8,255	10,232	11,046	11,386
4	9,333	9,533	11,597	11,212
5	4,823	8,530	11,541	11,460
6	11,123	8,617	11,336	11,260
7	11,051	11,598	11,686	11,241
8	5,773	7,818	11,288	11,428
9	8,527	8,021	11,126	11,406
10	10,255	10,190	10,878	11,444
Mean area	8,513	9,227	11,268	11,293
Mean dev.	1,545	929	236	132
Mean % dev.	18.2	10.1	2.1	1.2

substance which is known not to contain the unknown. The internal standard is added to the mixture in a definite amount and a series of samples run varying the percent of the unknown to be determined. The ratio of the intensity of the unknown to the intensity of the internal standard is plotted vs. the percent of the unknown to be determined and a working curve prepared. The primary requirements of the internal standard are that the line used for comparison occur within a few degrees of the line of the unknown, and that the internal standard have no lines which will reinforce the line of the unknown.

Sample preparation is extremely critical for the obtaining of reproducible and accurate results. In samples having constituents with excellent cleavage the substances tend to become oriented thus giving erroneous results. Sample preparation will be discussed further in the discussion of the procedure for this investigation.

Another important factor which is mentioned by Redmond (14) is the variation in the response of the Geiger tube from time to time and day to day. Redmond used a cemented tungsten carbide block to adjust the collimating slit system of the machine to obtain comparable re-

(14) Redmond, J. C., Quantitative Analysis with the X-ray Spectrometer, Anal. Chem. 19, p. 773-77, 1947.

sults from day to day.

On the machine used in this investigation it was found that the above factor was of extreme importance in reproducing results and the response of the Geiger tube varies considerably more than indicated by Redmond.

While the measurement of peak height or intensity and comparison with the height of the internal standard is very satisfactory for most quantitative analysis, the measurement of the area under the peak is the more accurate method of analysis. The area under the peak will be dependent among other factors on the particle size and on the number of the particles favorably oriented to give the diffraction. In this study the silica used for the determining of the standard curve was under five (5) microns maximum particle size. As shown by Alexander, this particle size allows results to be reproduced with very small error.

If two peaks having the same height are compared the one with the smallest particle size will have the greatest area. For most work this factor is not of too great importance as the particle size difference between the samples used to obtain the working curve and that of the unknown will be of the same magnitude. However, in a study of this type where new crystal phases are being formed, it is readily apparent that some of the crystals

formed will have a very small size. In this case the area under the peak will be appreciably more than in the case of particles of normal size.

Some investigators have measured the area under the peak using a planimeter, others have used a conventional method of expressing the area as the product of the peak height times the peak width at half maximum intensity or height, the height of the peak being measured above the background. The area in this case has no units but is strictly arbitrary.

In this study the area, in arbitrary units, was taken as the number of counts obtained when the sample being determined was rotated a certain number of degrees of arc. The number of degrees used being determined by the accuracy desired. The most accurate determination is to get a small amount of the background count on each side of the peak. This is not always possible as will be explained later.

The angle used in measuring the area under the most intense quartz peak was from two theta equals 27.5° to two theta equals 26° . This is approximately three-fourths of a degree on either side of the angle at which the maximum of the peak occurs.

The area under the cristobalite peak was measured in the above manner from two theta equals 22.5° to two theta equals 21.5° . This area is smaller than is actually desir-

able. However, it is not possible to measure a larger area due to the following:

Using CuK_α radiation the cristobalite maximum occurs at an angle $2\theta = 22^\circ-06'$, tridymite maximum at $2\theta = 20^\circ-44'$, third most intense tridymite peak at $2\theta = 21^\circ-35'$ and the second most intense line at $2\theta = 23^\circ-08'$, second most intense quartz line at $2\theta = 20^\circ-56'$. (The intensity values taken from the ASTM card index for x-ray patterns). As can be seen from the above data if a greater area is measured under the cristobalite peak than that from 22.5° to 21.5° the area measured will consist of part of the area contributed by the tridymite peaks. When low amounts of tridymite are present the area contributed by the second and third most intense lines is insignificant. However, as the percentage of tridymite present does increase to a point where the tridymite present is approximately equal to the cristobalite the error would become appreciable. In this investigation the percent of quartz and cristobalite in the sample was determined and the percent of tridymite plus glass determined by the difference between the sum of the quartz and cristobalite taken from 100 percent. In the case where the percent tridymite approaches the amount of cristobalite the percent of quartz and the percent of tridymite should be found and the cristobalite plus glass found by difference.

Figure 1* shows a graphical illustration of the above

discussion. One pattern is taken of a sample fired for ten hours at 1400°C and the other for forty hours at 1400°C. Of interest also is the difference in width at half maximum intensity between the quartz maximum and the cristobalite maximum. Also the increase in the tridymite peak can be observed.

* The second most intense line for quartz is masked by the tridymite peak and arrow indicates the position at which it occurs. The third most intense line for tridymite does not appear as the line is weak due to the small amount of tridymite present and due to its proximity to the relatively strong cristobalite peak.

Intensity

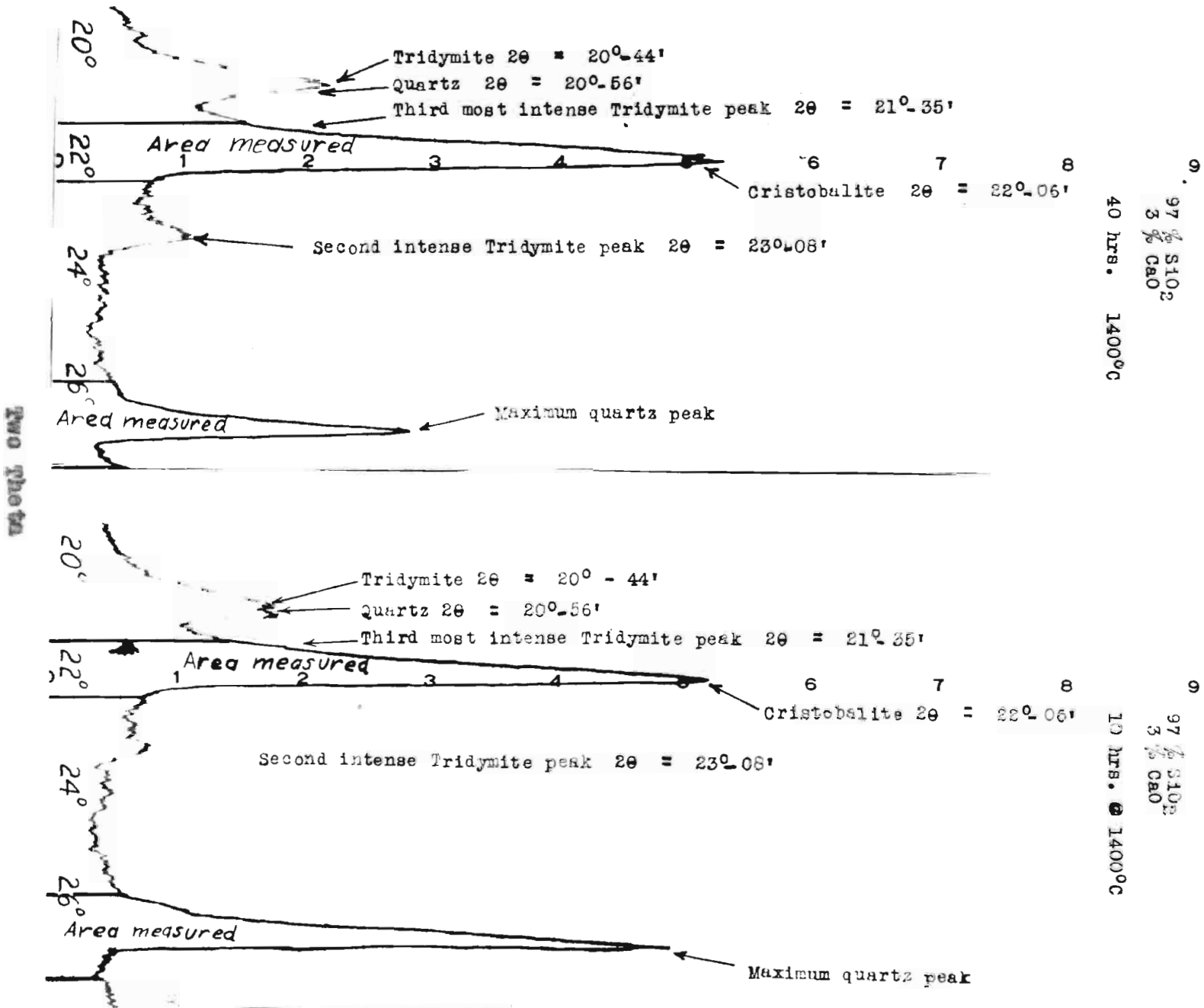


Figure 1. The relationship of the angles at which the diffraction maximum occur for cristobalite, tridymite and quartz in the range from two theta equals 27.5 to two theta equals 29°.

PROCEDURE FOR OBTAINING THE WORKING CURVE FOR
THE DETERMINATION OF THE PERCENT QUARTZ
AND CRISTOBALITE PRESENT IN FIRED
SILICA BRICK SAMPLES

The material used throughout this investigation was Ottawa sand having the following chemical analysis.

TABLE II

Chemical analysis of Ottawa Sand, analysis is of -5 micron material after leaching with hot 20% HCl solution.

SiO_2	97.68%
Al_2O_3	1.70%
Fe_2O_3	0.02%
TiO_2	0.19%
CaO	0.36%
MgO	0.05%

The Ottawa sand was ground in a porcelain ball mill until all the material would pass through a 325 mesh sieve. The time for particles greater than five microns to settle a definite distance was calculated using Stokes Law, and a 10% suspension of the -325 mesh silica was allowed to settle the calculated time and the material finer than 5 microns siphoned off. This procedure was repeated until a sufficient quantity of fine material was obtained.

The -5 micron silica was leached three times with a 20% hot solution of HCl and then thoroughly washed to remove the acid. In order to insure that all of the HCl was removed the silica was heated at 800°C for two hours.

To obtain the cristobalite for the preparation of the standard samples for the working curve, the -5 micron material was mixed with 3% CaO by grinding in a mortar until complete mixing was obtained. Using a platinum crucible as a container, the material was fired to 1500°C and held for five hours. After cooling the material was ground to pass through 325 mesh sieve and then reground until no grit was apparent. The purpose of the last grinding was to reduce the particles of the glass phase formed to the order of -5 microns or less. A sample of this material was checked on the x-ray machine and the only crystal phase found to be present was cristobalite.

The samples for determining the working curve were prepared using the cristobalite and the minus five micron silica. All weighings were made on an analytical balance. These samples were thoroughly mixed by grinding in a mortar. It is of extreme importance that the samples be completely homogenous. If they are not mixed thoroughly it will be impossible to reproduce the results on different samples of the same mix.

Standardization of X-Ray Equipment:

As pointed out previously in the section on Quantita-

tive Analysis by X-Ray Methods, the response of the Geiger tube is not constant over a period of time. When readings must be compared from day to day some means of keeping the machine standardized must be used to allow comparison of the results obtained at the different times. The procedure used for the standardizing of the x-ray machine in this investigation is as follows.

The machine is turned on and allowed to warm up for at least one hour, before any adjustments of the collimating system are made. A piece of brass was used as the standardizing sample. The brass has a very intense peak occurring at approximately two theta equals $49^{\circ}-10'$. Using the one rpm drive motor for the goniometer arm, a Geiger tube slit of minimum width, a Geiger tube wedge at No. 2 position, #64 scale ratio, and the tube slit at medium width, the tube wedge is adjusted to give a count of $700 \pm 1\%$ when the brass sample is rotated from two theta equals 50° to two theta equals 48° . The settings and the sample used are strictly arbitrary and any count could be used to check the machine as long as the same procedure that is used to prepare the working curve is used on all the quantitative analysis work for which the working curve is used. However, care must be taken to see that the counting rate at the peak maximum does not exceed 1200 counts per minute which is the maximum counting rate for the mechanical impulse counter. The maxi-

num rate using the above settings was in the order of 900 counts per minute at the brass peak maximum.

Preparation of X-Ray Samples

Several methods have been suggested for the preparation of the samples to be used for quantitative analysis by x-ray methods. In this work the sample holder used was made of aluminum and was made similar to that used (15) by McGreary.

In preparing the samples the sample holder is placed face down on a glass plate and held firmly against the glass so that the face of the sample will be in the same plane as the sample holder face. The sample material is then placed in the well of the sample holder from the back and packed in firmly. A slight excess of sample material is used and the excess shaved off with a razor blade. The back of the sample is covered with a glass microscope slide to prevent the holding clip on the specimen post from knocking the sample out when the sample is placed in position for running.

The standardization of the x-ray machine was checked and if necessary the proper adjustments made. The sample was then placed in position on the specimen post and the

(15) McGreary, G. L., Improved Mount for Powered Specimens Used on the Geiger Counter X-Ray Spectrometer. Jour. Am. Cer. Soc. 32, No. 4, pp. 141-46, 1949.

area under the quartz and cristobalite peaks measured using the method given on page 18 of this thesis. Five separate samples of each mix was prepared and the respective areas of the quartz and cristobalite peaks measured three times for each sample. The maximum error of the average of any one sample from the average of the five samples was under 2%

The working curve is shown in Figure 2. It will be noticed that the curves are not straight lines but are slightly curved. This is due to the response of the Geiger tube not being perfectly linear as the counts or intensity is increased. The effect of increasing the energy input into the Geiger tube and the counting rate response of the Geiger tube is shown graphically by Friedman.⁽¹⁶⁾ The curves do not show a zero area for the zero percent of either quartz or cristobalite. The count shown represents the area beneath the background between the respective angles used for the quartz and cristobalite.

(16) Friedman, H., Geiger Counter Spectrometer for Industrial Research. Electronics 28, No. 4, p. 132, 1945.

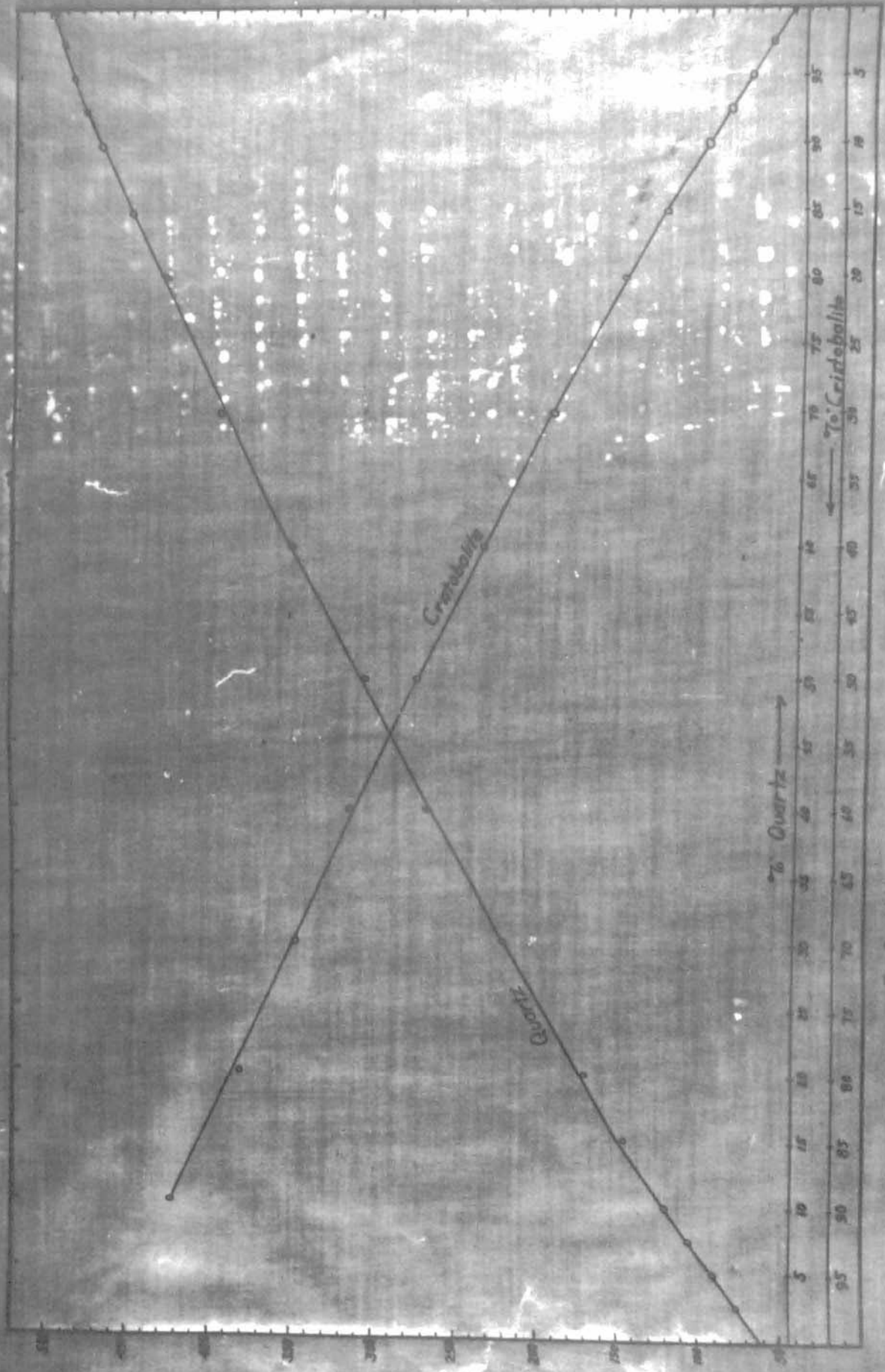


Fig. 2. Working curve to determine % Quartz & Cristobalite.

PRELIMINARY INVESTIGATION OF THE EFFECT OF TITANIUM
DIOXIDE IN SILICA BRICK

The purpose of the preliminary investigation was to study the effects of additions of titanium dioxide on silica brick samples by firing the samples to the desired temperature and after soaking for a predetermined time drawing the samples and determining the amount of quartz conversion to tridymite and cristobalite. The analysis was made by the x-ray method already described.

Samples of silica brick were prepared using Ottawa sand of the following chemical analysis.

TABLE II-a. Chemical Analysis of Ottawa Sand
as Received.

SiO ₂	98.28%
Al ₂ O ₃	1.10%
Fe ₂ O ₃	0.02%
TiO ₂	0.19%
CaO	0.36%
MgO	0.05%

Two size ranges of the above material were used, 50% -20 +30 mesh and 50% -40 +80 mesh. Using this material the following samples were prepared:

TABLE III

Composition of Silica Brick Samples Prepared to Study the
Affect of Additions of Titanium Dioxide

<u>Sample</u>	<u>% SiO₂</u>	<u>% CaO</u>	<u>% TiO₂</u>
1	97	3	0
2	96	3	1
3	95	3	2
4	94	3	3
5	93	3	4
6	92	3	5

Calcium oxide was added to the batch as chemically pure (C.P. Grade) calcium carbonate and titanium dioxide as chemically pure (C.P. Grade) titanium dioxide. Samples were prepared by grinding in a mortar until the constituents were thoroughly mixed. Sufficient water was then added for dry pressing and the sample remixed. Samples were formed into cylinders approximately one inch in diameter and containing approximately 30 grams of mixture. A carver laboratory press and steel mold was used to form the samples, and pressure used was in the order of 500 lbs per square inch.

The samples were then fired to 1400^oC in an electric furnace. Samples from each mix were drawn after holding at 1400^oC for 20 hours. sample containing no titanium

dioxide were drawn every five hours and those containing titanium dioxide were drawn every ten hours. Total soaking time for the last samples drawn was 65 hours.

X-ray patterns were run on some of the samples and all were found to be completely converted to cristobalite. The furnace used is controlled by a Leeds and Northrup Micromax controller, and upon checking it was found that the actual temperature of the firing was 1470°C or above.

The above mixes were again prepared and fired to 1300°C . The temperature was checked periodically using an optical pyrometer. Samples were drawn on the same schedule as before.

Results of 1300°C Firing:

The results of the analysis of the samples fired for twenty-five and sixty-five hours are presented in Table IV, page 27. The results were obtained by quantitative analysis by x-ray using the procedure given for obtaining the working curve.

Discussion of the Results Obtained on 1300°C Firing Presented in Table IV.

It will be noticed that the plus and minus deviation from the average of the five samples run on the quartz determination is in some instances quite large. This is due almost entirely to the samples not being ground to a fine enough particle size. The results obtained for the

TABLE IV

Analysis of silica brick samples fired to 1300°C for 25 and 65 hours.

Time Hrs.	Temp. °C	% TiO ₂ Add.	% Quartz	% Crist.*	% Glass Trid.**	Max. Deviation of any Sample from Average 5 Samples			
						QUARTZ		CRIST.	
						+	-	+	-
25	1300	0	79.0	6.5	14.5	1.6	1.2	--	--
25	1300	1	76.2	11.0	12.8	--	--	--	--
25	1300	2	77.5	12.5	10.0	1.5	1.5	--	--
25	1300	3	74.6	12.5	12.9	4.8	3.0	--	--
25	1300	4	72.5	9.5	18.0	3.1	3.7	--	--
25	1300	5	69.8	6.0	24.2	2.4	1.8	--	--
65	1300	0	79.0	8.2	12.8	1.5	1.0	--	--
65	1300	1	74.0	12.0	14.0	5.2	5.8	--	--
65	1300	2	70.3	13.5	16.2	1.2	2.2	--	--
65	1300	3	72.6	13.5	13.9	2.6	3.0	--	--
65	1300	4	74.3	10.0	15.7	5.2	5.1	--	--
65	1300	5	71.5	8.0	20.5	1.1	1.3	--	--

* Cristobalite

** Tridymite

crystalite are excellent, all deviations of any one sample being less than one-half of one percent from the average. The explanation for this is that the crystalite formed is of very small crystal size and the grinding has very little effect in reducing the size of the crystalite crystals.

In the samples fired for 25 hours there is no increase in the tridymite and glass phase until the additions of TiO_2 was four and five per cent. There is very little change in the amount of conversion of the quartz and the conversion seems to be taking place in changing the crystalite formed over to the tridymite phase. The change is not appreciable in any of the samples tested that were fired to $1300^{\circ}C$. The results are erratic and the only conclusion that can be drawn is that there is an increase in tridymite in the samples containing four and five per cent of titanium dioxide.

DESIGN AND BUILDING OF THE HIGH TEMPERATURE
X-RAY FURNACE

Originally it was intended to do all the work on this problem using a high temperature x-ray furnace and studying the various reactions at the normal firing temperatures. By this method it was hoped to obtain a better knowledge of the actual rate of the reactions and to determine the best temperature suitable for the highest rate of conversion of the quartz over to tridymite.

The following is a description of the X-ray furnace designed and built to study the problem.

Figure 3 shows a crosssection of the furnace. The cooling jacket of the furnace is made of brass pipe, the outer pipe being four inches (4") in outside diameter and the inner pipe being three (3") inches in diameter. Due to the small space or distance between the x-ray tube slit system and the sample holder it was necessary to cut a section out of the outer cooling jacket to allow the furnace to be put in place. A $3/8"$ x $1/8"$ opening is cut in the inner pipe to provide for the entrance of the primary x-ray beam into the furnace. This opening is covered by a beryllium metal window $1/32"$ in thickness.

At the top of the furnace is a solid brass rod with holes drilled for the thermocouple and lead wires to the heating muffle. The brass parts of the furnace are cooled

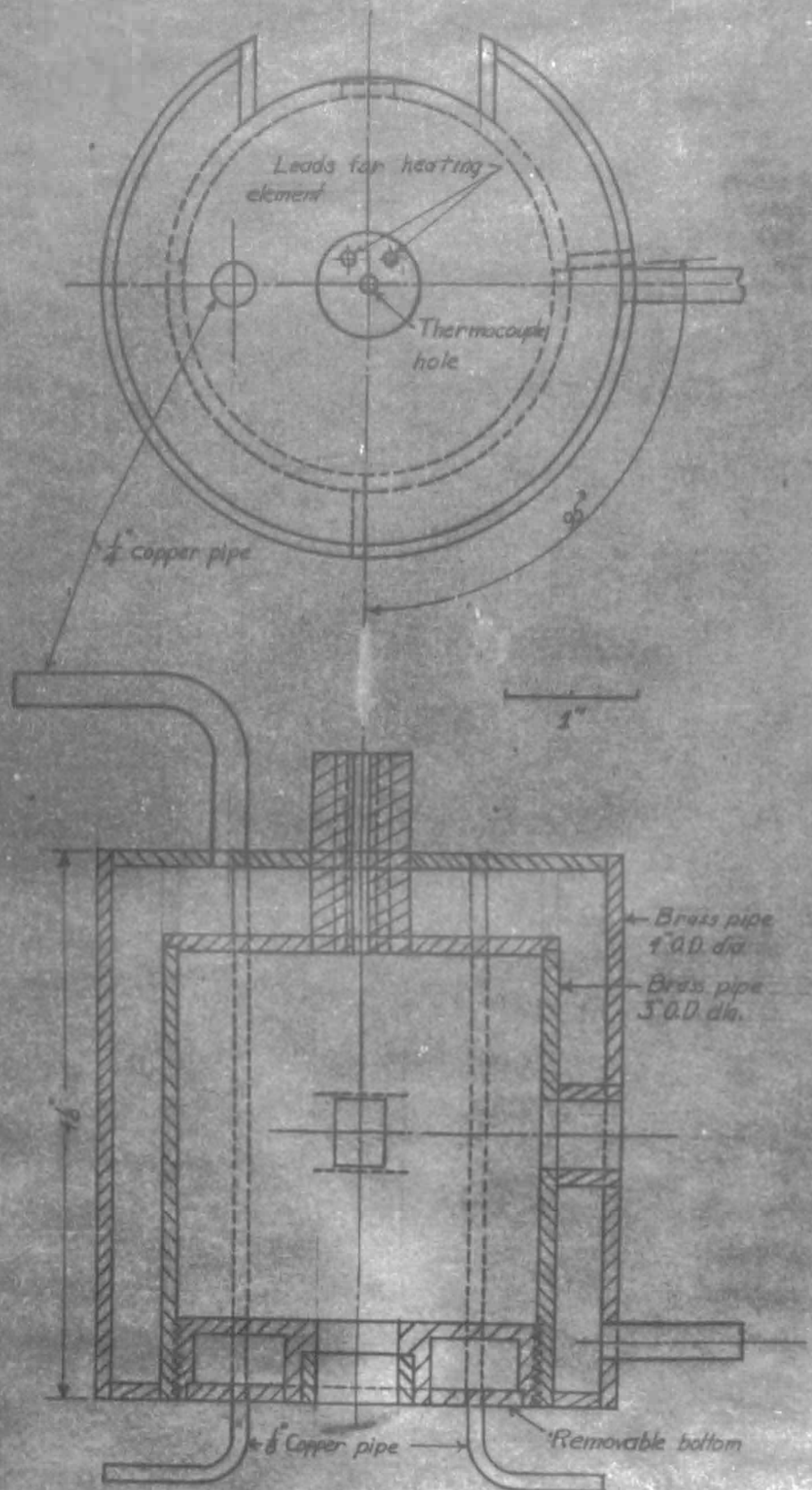


Fig. 3. Crosssection of brass cooling jacket for x-ray furnace.

by circulating water through the cooling jacket. The brass bottom of the furnace is removable to allow access to and for the installation of the heating element. The bottom is also water cooled.

A section, 95 degrees in arc, is cut from the cooling jacket to allow complete diffraction patterns to be run at high temperatures. When the furnace was designed it was intended to use beryllium to cover this window also. However, beryllium metal is so brittle that it cannot be bent and the cost of a curved section to fit the opening was too prohibitive for beryllium to be used.

The heating element (Fig. IV) is made by winding #22 gauge platinum, 20% rhodium wire on the inside of a cast alumina muffle. The alumina muffle was first cast then fired until sufficient strength was obtained so that the slots and holes for the winding could be cut and drilled. The section of the furnace that is in contact with the removable bottom is made of a cast piece using 50% alumina slip with 50% wood sawdust on a volume basis. The groove for the muffle is then cut after the piece has been fired and has sufficient strength for handling.

MgO is used to insulate the heating muffle from the inner wall of the brass cooling jacket. To aid in cooling the part of the furnace immediately in front of the x-ray tube slit system, compressed air is blown between the furnace and the slit system.

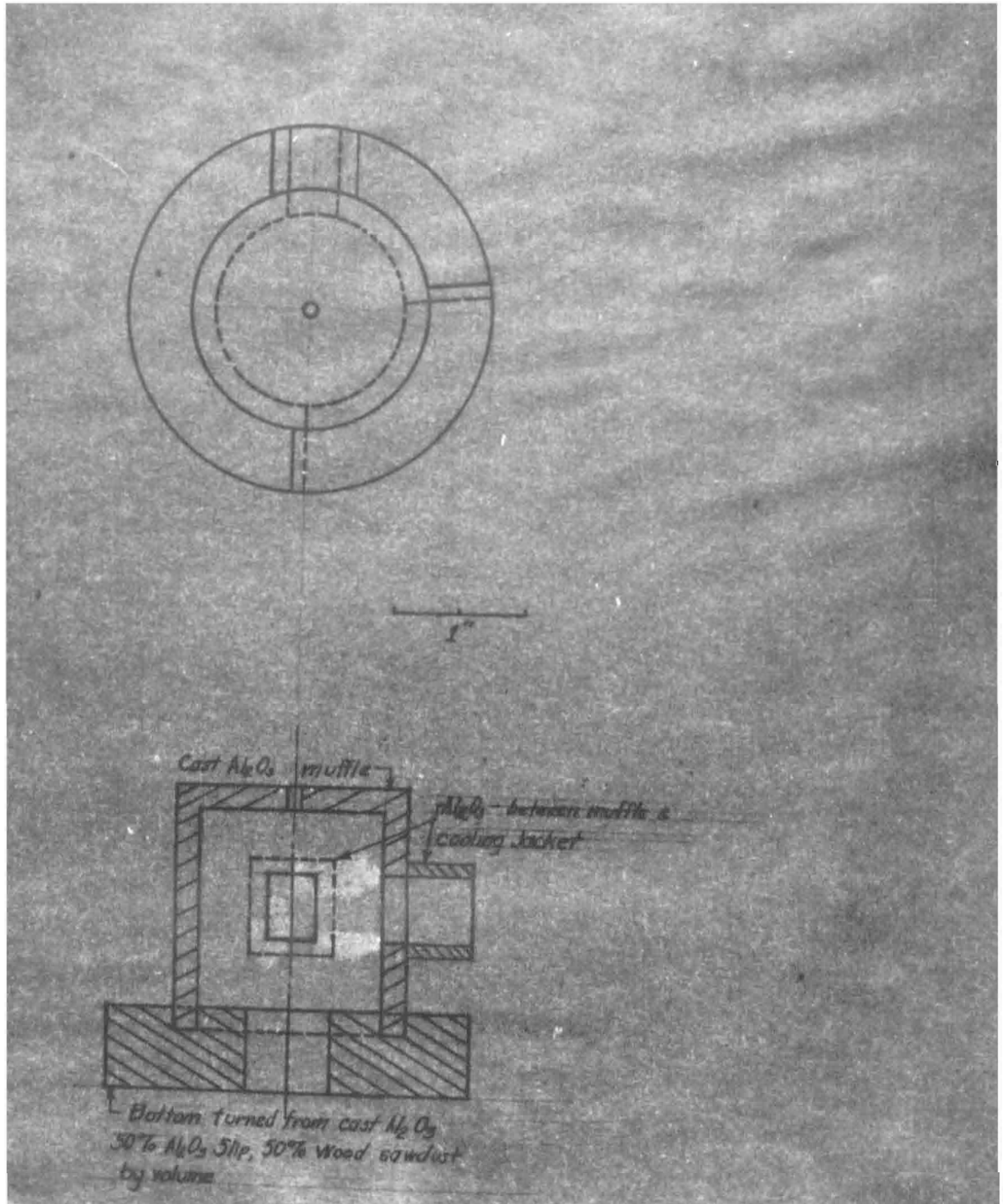


Fig. 4. Crosssection of Alumina refractory heating element.

When designing the furnace it was realized that there would be an enormous heat loss due to the small amount of insulation that could be used between the brass cooling jacket and the heating muffle. For this reason the wire of the heating element was placed on the inside surface of the heating element to obtain the greatest amount of insulation and the most efficient heating. It was thought that this method would allow the desired temperatures to be reached without having to keep the temperature of the wire at a temperature much higher than that of the sample.

The part of the sample holder which fits inside the heating muffle is made of alumina. A solid alumina blank is first cast and fired to a high enough temperature to obtain sufficient strength for handling and still allowing it to be machined down to the correct size. Shrinkage is allowed for and the sample turned down to the correct size using a metal lathe. The portion which is cut away must be as nearly on the center line of the post as possible. If this part is off center it will be impossible to align the post to enable accurate, complete patterns to be run. A template made by drilling a section of steel pipe out to the correct size to fit the post, was used to obtain the exact center of the post. The "dovetailed" sample well was then cut in the post and the post fired to approximately 1700°C to obtain the required

strength for use in the furnace.

To prevent reaction of the sample with the post at high temperatures a piece of sheet platinum was cut and formed to fit the sample well in the post. The dimensions of the sample well in the post are $\frac{1}{8}$ " wide, $\frac{3}{4}$ " high and approximately $\frac{1}{8}$ " in depth. The post made for the furnace was accurate enough that the standard or normal specimen post and the alumina post could be interchanged without realigning the x-ray machine. The angle at which the $3.35A^{\circ}$ maximum of the quartz sample occurred using the alumina post was 3 minutes in degrees theta greater than with normal post. It is difficult to align the x-ray machine closer than ± 0.05 degrees theta.

CONTROLLING EQUIPMENT

Power is supplied to the furnace by means of an auto transformer. The transformer is manually operated in raising or lowering the temperature. When the desired temperature is reached, the temperature is held constant (2°C) by a Leeds and Northrup Speedomax Type G Recorder, in conjunction with a Leeds and Northrup M. E. C. Unit.

The details of the furnace and general setup of the furnace on the x-ray machine may be seen in the photographs of the furnace and x-ray machine on the following pages.

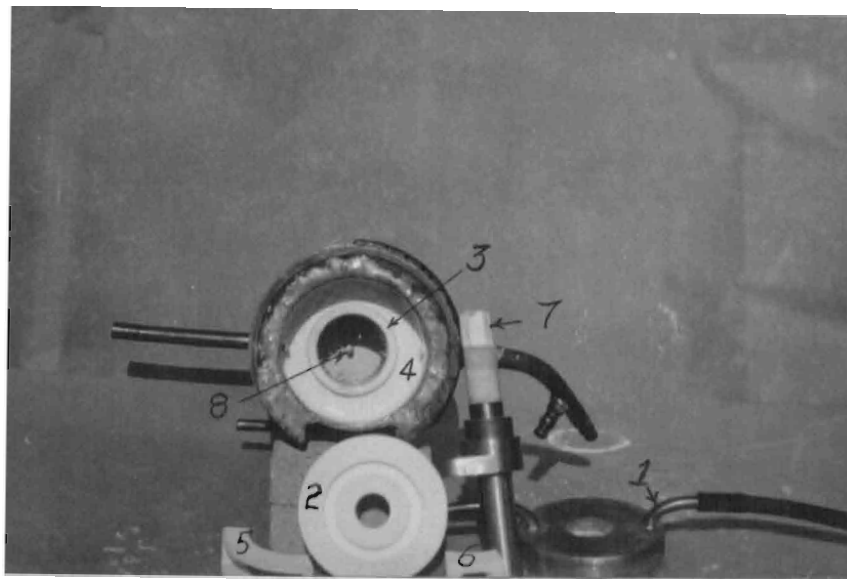


Figure 5. Photograph of the furnace showing the refractory parts of the furnace and installation in the furnace.

1. Bottom.
2. Alumina insulator bottom.
3. Muffle.
4. MgO insulation.
5. Alumina lip which fits between muffle and inner wall of cooling jacket (95° arc).
6. Alumina lip which fits between the muffle and cooling jacket (entrance of x-ray beam).
7. Alumina sample holder post.
8. Thermocouple.



Figure 6. General setup of the x-ray furnace and controlling equipment.

1. Water connections and outlet.
2. Thermocouple leads. (Thermocouple is Pt.+Pt. 10% Rh.)
3. Power supply cable.
4. Leads and Northrup Recorder Controller.
5. M. E. C. Unit.
6. Auto transformer.
7. Spectrometer recorder.
8. Airline.



Figure 7. The above photograph shows the furnace in place on the x-ray machine. No. 1 points out the mechanical counter that is used in conjunction with the recorder to run quantitatively the amounts of the various polymorphic forms of silica present in the sample.

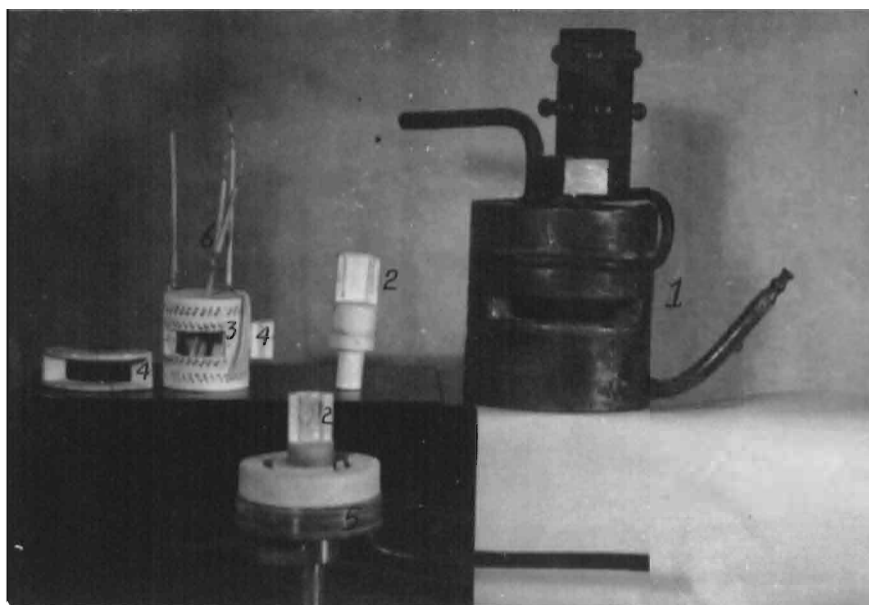


Figure 8. Furnace disassembled.

1. Brass cooling jacket
2. Al_2O_3 sample holder
3. Heating muffle
4. Al_2O_3 lips (Fitted between the inner wall of cooling jacket on heating element.)
5. Removable bottom
6. Thermocouple

PROCEDURE FOR STUDYING THE RATE OF CONVERSION OF QUARTZ
TO TRIDYMITITE AND CRISTOBALITE AT HIGH TEMPERATURES
USING THE X-RAY FURNACE

The x-ray machine is standardized using the same procedure as that used in running quantitative analysis at ordinary temperatures. (see p. 19)

After the machine is standardized the normal specimen post is removed and the alumina sample holder placed in position on the x-ray machine. The area under the maximum quartz peak is then measured using the same procedure as in obtaining the working curve. (The area is measured before firing in order to compare the result after firing.)

The post is then placed in the furnace and the thermocouple adjusted to a height that will just allow the junction to be imbedded in the top of the sample. The temperature is then raised at the rate of 500°C per hour until the desired temperature is obtained.

The standardization of the x-ray machine is checked and necessary adjustments made if needed. The furnace is immediately placed in position on the x-ray machine and the area under the quartz and cristobalite peaks measured. It was found that at a temperature of 1300°C the angle at which the maximum of the quartz peak occurs is about 20 minutes in 2θ less than at room temperature. The area

measured under the quartz peak was from two theta equals 27° to two theta equals 25.5° . The area measured under the cristobalite peak was from two theta equals 22.25° to two theta equals 21.25° . Each area was measured five times and the average taken. Total time needed to measure the two areas is approximately twenty minutes. After the areas are measured the furnace is removed and the standardization checked. Considerable care is needed in placing the furnace on the x-ray machine and in removing, not to change the x-ray intensity by disturbing the wedge setting.

To provide a check for the above procedure a sample of MgO, which is known to have no inversions at the higher temperatures, was run. The results are presented in Table V. (p. 42)

Using CuK_{α} radiation the most intense peak for MgO occurs at an angle of two theta equals $42^{\circ}-48'$ and the area under the peak was measured from two theta equals 43° to two theta equals 41.5° . (At 1000°C the peak maximum occurred at an angle of $2\theta = 42^{\circ}-37'$, and at $42^{\circ}-15'$ at 1300°C .)

From Table V it is seen that excellent results were obtained while holding the sample at 1000°C for four hours. When the temperature was raised to 1300°C the count decreased by 9.3%. This decrease is due almost entirely to the sample shrinking. When the sample shrinks and the face of the sample is no longer on the focusing circle for

TABLE V

Results of measuring the area under the MgO maximum from $2\theta = 43^\circ$ to 41.5° after the sample had been held at temperatures and times as tabulated.

Time	Temp.	M G O P E A K		Remarks
		Area Av. 5 Rdgs.	Peak Angle 2θ	
10 min	1000°C	367	42°-35'	
52 min	"	365	"	
1 hr 35 min	"	365	"	
4 hr	"	365	"	
4 hr 45 min	1300°C	331	42°-15'	Sample Shrink- ing
2 hr 50 min	"	331	42°-12'	
4 hr 20 min	"	323	42°-10'	
5 hr 15 min	"	326	42°-10'	

the x-ray beam and Geiger tube, the effect is the same as if the machine was out of alignment, and the intensity decreases. After the sample was held at 1300°C for 45 minutes the count or area measured was again constant. The variation in area measured is less than 2% for the five hours that the sample was held at 1300°C .

In view of the excellent results obtained in running the sample of magnesia it was believed that the problem of obtaining reproducible results was solved and a sample of the minus five micron silica was run. The procedure used has been described and need not be discussed again.

Results of the Study of the Rate of Conversion of Silica
By Means of the High Temperature X-Ray Furnace.

The results of this study are presented in Table VI, (p. 43). The area of the quartz peak was measured with the furnace off the post and with the furnace in place. The beryllium window reduces the intensity of the primary beam approximately twenty-five percent. The area measured for the quartz peak immediately upon obtaining 1300°C is 2.91% less than that measured at room temperature. This decrease is due to the decrease in scattering power of the atoms due to the increased thermal vibration of the electrons at the high temperature.

Figure IV shows graphically the decrease in area of

TABLE VI

Result of measuring the area under the quartz maximum peak from $2\theta = 27^\circ$ to 25.5° and the area under the cristobalite maximum peak from $2\theta = 22.5^\circ - 21^\circ$, at 1300°C after the sample had been held at the temperature for time as tabulated.

Time	Temp.	SILICA PEAK		CRISTOBALITE		Remarks
		Area Av. 5 Rdgs.	Peak Angle 2θ	Area Av. 5 Rdgs.	Peak Angle 2θ	
---	---	503	$26^\circ-43'$	---	---	
---	---	378	"	---	---	Furnace in place
20 min	1300°C	367	$26^\circ-35'$	58	---	
2 hrs 30 min	"	291	"	125	$21^\circ-45'$	
5 hrs 30 min	"	245	"	172	"	
7 hrs 55 min	"	229	"	189	"	
10 hrs. 25 min	"	196	"	187	$21^\circ-45'$	
---	room	301	$26^\circ-52'$	311	$22^\circ-02'$	

the quartz maximum and increase of the area of cristobalite maximum as a function of the firing time at 1300°C. The curve is self explanatory and needs no explanation.

If it is assumed that the area underneath the peak is directly proportional to the amount of quartz present the amount of quartz remaining after firing may be calculated. (That this assumption is not entirely true has been shown in the preparation of the working curve for analysis at ordinary temperatures.)

However, with the above assumption the amount of quartz present after firing will be:

$$\% \text{ quartz} = \frac{301}{503}$$

$$= 59.8\%$$

As a further check on the above result the initial and final counts at 1300°C may be used:

$$\% \text{ quartz} = \frac{196}{367}$$

$$= 53.5\%$$

This gives a difference of 6.3% in the amount of quartz present after firing. This difference is to be expected due to the assumption made and the fact that some of the quartz had been converted when the initial reading was taken.

Making a further assumption that the average of the above result is the correct amount of quartz present after

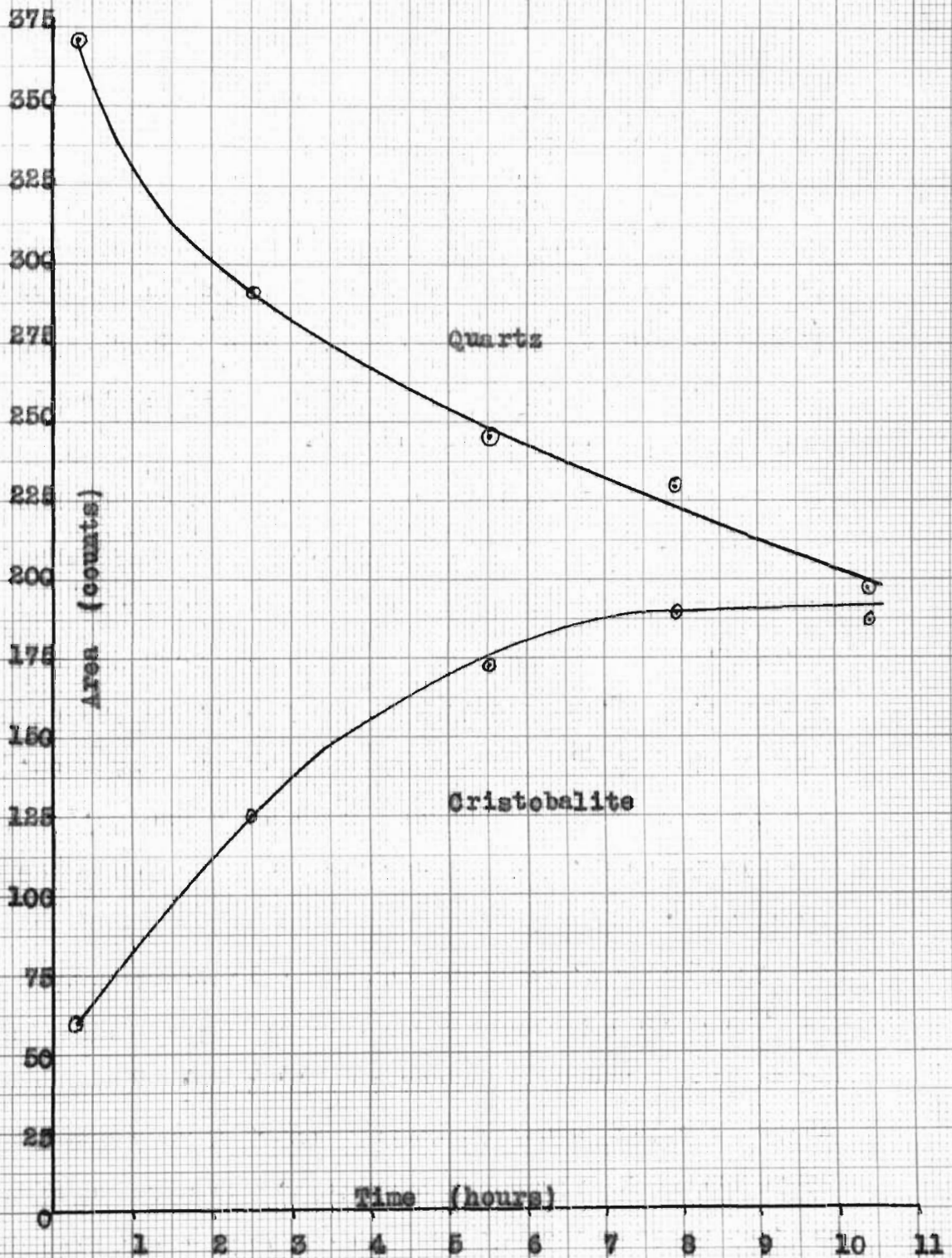


Figure 9. plot of area vs. firing time for
-5 micron silica. (Areas measured at
1300°C.)

firing, then 43.4% of the quartz has been converted to cristobalite and tridymite.

In view of the fact that no flux was added to the material this result appears to be high for the time fired and the temperature used. The small particle size of the material used and the direct radiation of the platinum wired heating element of the furnace are probably due to some extent to the apparent large conversion of the quartz.

As mentioned previously on the design and building of the furnace the space in which to insulate the heating element was very limited. To raise the temperature of the sample to 1300°C the platinum + 20% rhodium wire used to heat the sample was at such a high temperature that when the furnace was held at 1300°C some vaporization of the platinum occurred. This platinum was deposited on the surfaces inside the muffle which were at lower temperature than the wire. Consequently some of the platinum was deposited on the surface of the sample. Platinum has a very high absorption factor for x-rays and it was thought that this factor might be decreasing the intensity received by the Geiger tube thus making it appear that the area under the quartz maximum was decreasing.

For this reason the wiring was coated with a thin layer of Al_2O_3 slip to eliminate the vaporized platinum in the furnace atmosphere. It was realized that this would decrease the efficiency of the heating element and would in-

crease the heat lost to the cooling jacket.

After coating the windings with the slip another run was attempted. The heat loss was so great that in obtaining the temperature of 1300°C the wire melted after about one hour at 1300°C .

There was not sufficient time remaining to rebuild the furnace and complete the investigation in the manner described above.

The procedure described for the studying the rate of the conversion of the quartz at the actual temperatures was developed after several trials of other methods and is believed by the writer to be a satisfactory method and by modifying the present furnace some valuable information could be gained using this method of approach on this problem.

CONTINUATION OF PRELIMINARY INVESTIGATION

Samples as listed in Table III were prepared in the same manner as in the preliminary investigation with the following exception. C.P. grade calcium carbonate was calcined at 1000°C and converted to calcium oxide. The calcium oxide was added to the samples in place of the calcium carbonate as used in the preliminary investigation.

The samples were fired in an electric furnace, the temperature being 1400°C . Samples were drawn every ten hours until the total time on the last samples drawn was 40 hours. The temperature of the furnace was checked periodically using an optical pyrometer.

Immediately after drawing the first samples, a quantitative x-ray analysis was made on the sample containing no titanium dioxide, and it was found to be composed of 50% cristobalite, 36.2% unconverted quartz and 13.8% tridymite and glass. Apparently this rate of conversion was so rapid that any further heating would not have given a thorough study of the effect of titania as a mineralizer. Therefore after thirteen hours at 1400°C the temperature was lowered to 1350°C for the remainder of the firing.

The analysis of the samples are presented in Table VII, page 49 and were obtained by the x-ray quantitative analysis method. The procedure used was the same as that for preparing the working curve, page 17

TABLE VII

Analysis of silica brick samples fired to 1400°C and 1350°C from 10 to 50 hours.

Time Hrs.	Temp. °C	% TiO ₂	% Quartz	% Crist.*	% Glass † Trid.**	Max. Deviation of any sample from Average 5 Samples			
						Quartz		Crist.	
						+%	-%	+%	-%
10	1400	0	36.2	50.0	13.8	1.8	2.4	---	---
"	"	1	27.0	53.6	19.4	3.0	1.2	1.0	---
"	"	2	27.8	50.2	21.0	0.8	1.0	1.0	0.8
"	"	3	34.1	51.5	13.4	1.9	1.5	1.9	0.9
"	"	4	24.2	51.0	24.8	1.0	1.0	---	0.6
"	"	5	25.8	44.5	31.7	1.8	1.0	1.5	---
13	1400								
7	1350	0	24.0	57.5	19.5	2.4	2.2	---	---
"	"	1	18.8	59.4	21.8	0.8	1.0	0.6	---
"	"	2	18.0	53.6	28.4	1.2	1.6	2.6	---
"	"	3	24.0	52.6	23.6	1.8	1.4	1.6	1.2
"	"	4	17.2	50.5	32.3	0.8	1.0	0.7	1.1
"	"	5	17.8	50.0	32.2	---	1.4	1.2	1.1

* Cristobalite

** Tridymite

TABLE VII (Contd.)

Time Hrs.	Temp. °C	% TiO ₂	% Quartz	% Crist.	% Glass + Trid.	Max. Deviation of any sample from Average 5 Samples			
						Quartz		Crist.	
						+	-	+	-
13	1400								
17	1350	0	20.0	58.0	22.0	1.0	0.8	0.6	1.4
"	"	1	14.5	55.9	29.3	1.5	1.2	1.0	---
"	"	2	16.4	53.4	30.4	1.2	0.6	1.6	1.6
"	"	3	24.8	56.0	19.2	1.0	0.6	0.8	---
"	"	4	16.0	51.6	32.4	0.8	---	1.6	1.4
"	"	5	17.2	48.0	34.8	0.8	1.2	0.8	1.4
13	1400								
27	1350	0	19.0	59.5	21.5	3.0	2.0	1.5	2.5
"	"	1	14.8	55.4	29.8	---	0.8	0.6	0.8
"	"	2	17.0	54.2	28.2	1.8	---	---	---
"	"	3	24.0	55.0	21.0	1.6	2.0	---	0.6
"	"	4	16.0	49.8	34.2	---	1.2	0.6	---
"	"	5	16.0	46.4	37.5	0.6	0.8	0.8	0.6

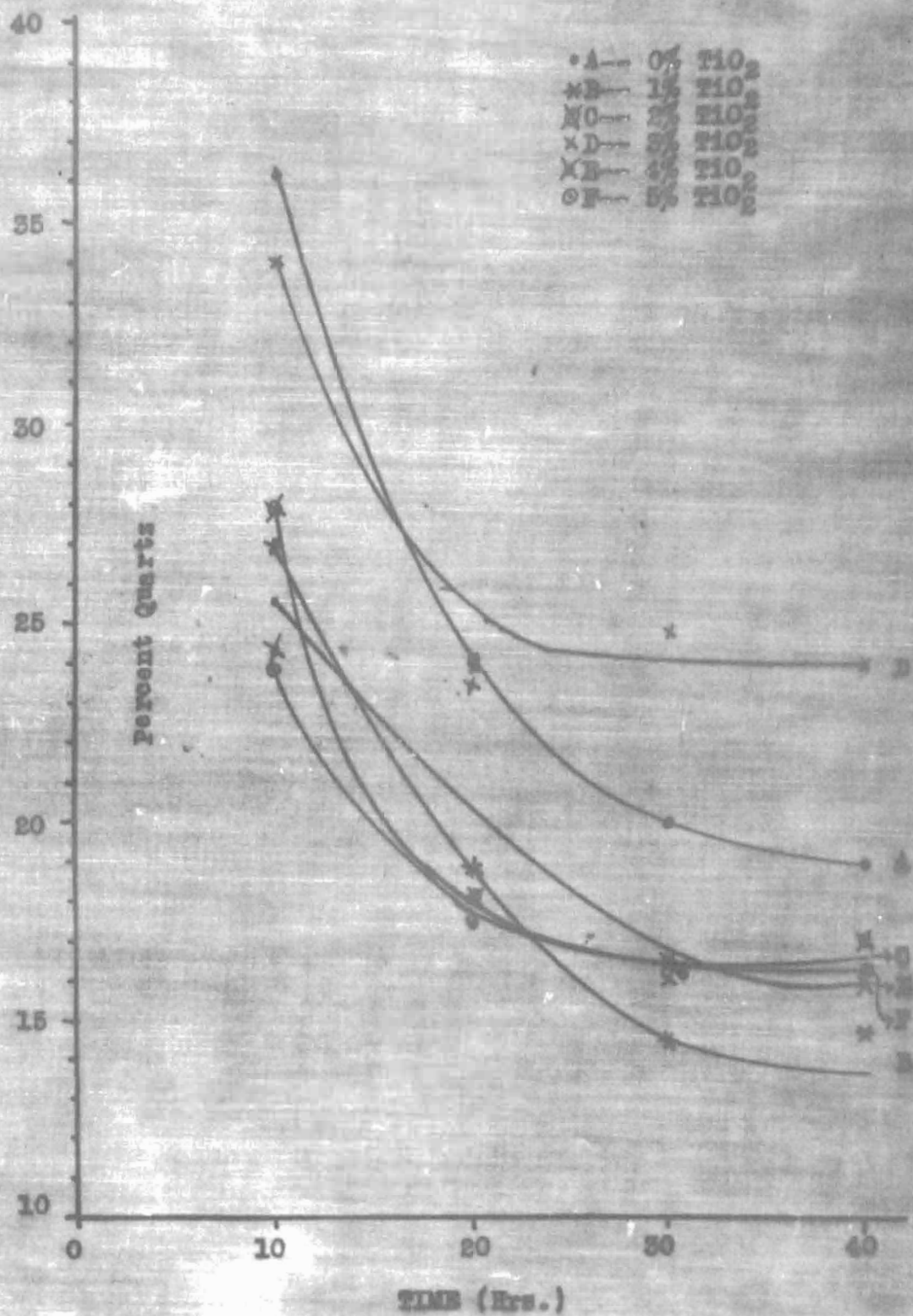


Figure 10. Graph 1. Effect of additions of titanium dioxide and soaking time on the conversion of quartz to cristobalite and tridymite. (data of Table VII)

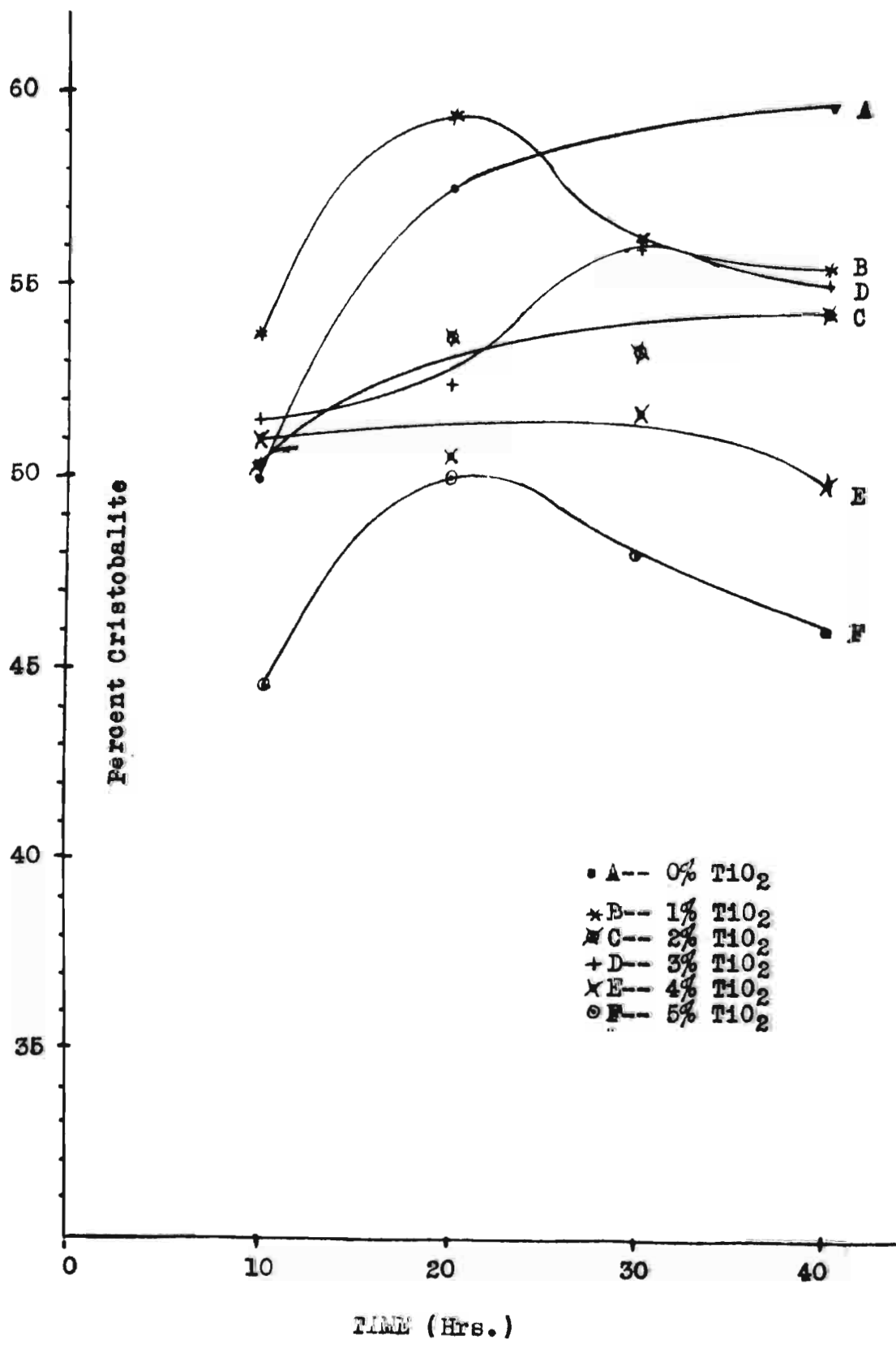


Fig. 11, Graph 2. Effect of additions of titanium dioxide and soaking time on the formation of cristobalite. (data of Table VII)

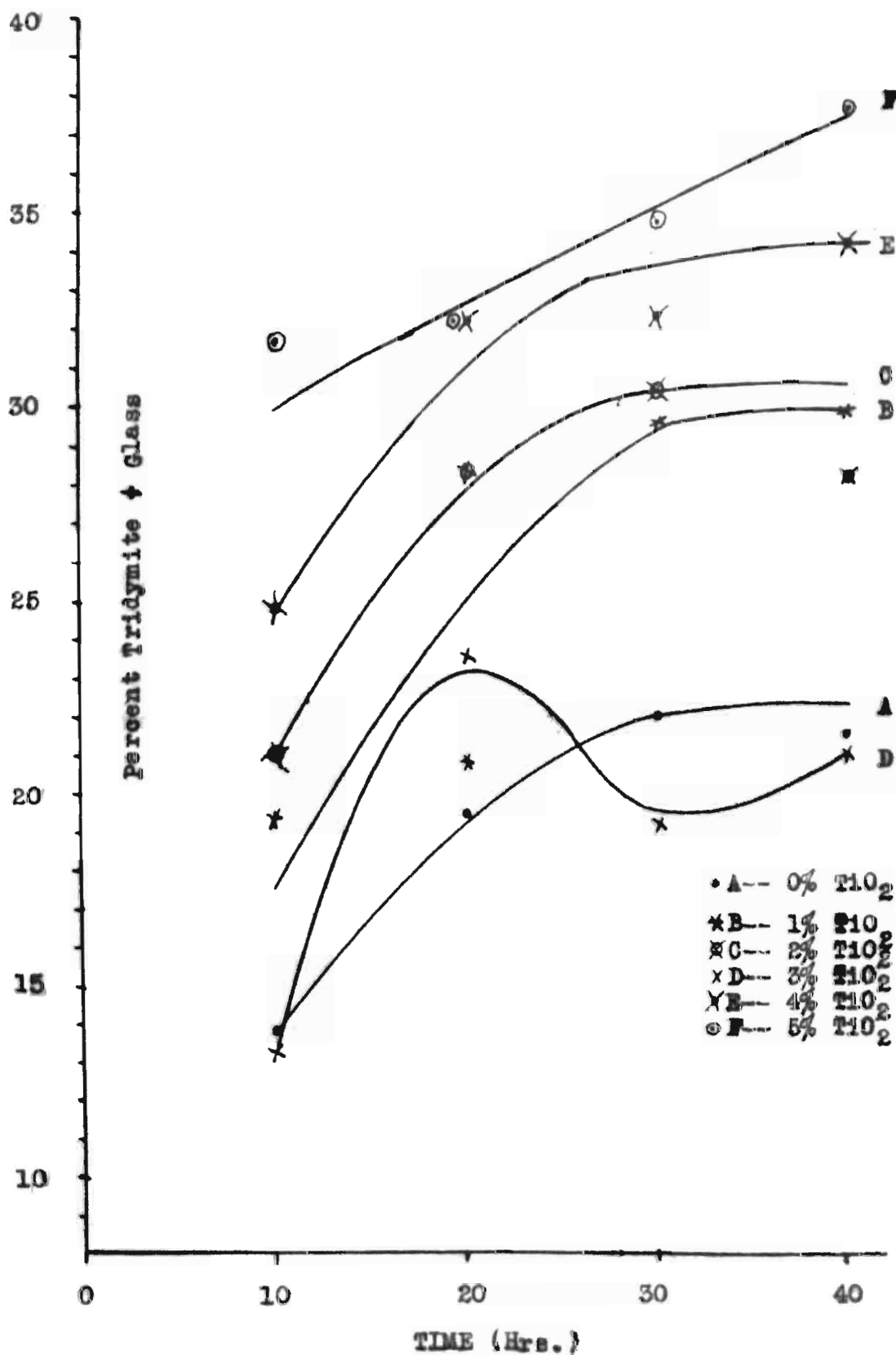


Fig. 12, Graph 3. Effect of additions of titanium dioxide and soaking time on the formation of Tridymite + Glass. (data of Table VII)

DISCUSSION OF RESULTS OBTAINED ON SILICA

BRICK SAMPLES FIRED TO 1400°C

The tabulated results are presented in Table VII, page 49, and are shown graphically in Graphs 1, 2 and 3.

Upon examination of graph No. 1, it is observed that all mixes with the exception of the 3% TiO_2 mix have less quartz remaining in the fired sample than did the standard mix, of 97% SiO_2 and 3% calcium oxide. There is no appreciable decrease in the amount of quartz present between the amount of quartz present, when one percent TiO_2 is added or when five percent TiO_2 is added at the longest firing time of 40 hours. However, at the 10 hours firing time the difference is approximately 12% for the five percent addition of TiO_2 , based on the amount of quartz present in the sample originally. The quartz has decreased approximately seven percent more than the standard mix due to the five percent addition of TiO_2 . On the basis of comparison of the amount of quartz originally present it appears that the additions of 1, 2, 4 and 5 per cent TiO_2 has little effect on the conversion of the quartz. However, the amount of the cristobalite and tridymite present must be studied before any conclusions can be drawn. The effect of the addition of three percent TiO_2 will be discussed after all three graphs are

compared and discussed.

Graph No. 2 shows the percentage of cristobalite present in the fired samples for the various mixes and firing times. In all cases with the exception of the one percent addition, there is less cristobalite present than with the standard mix. For the first 20 hours firing time the one percent TiO_2 mix has more cristobalite formed than does the standard mix. However, it is not greater than two percent and probably is within the limits of the accuracy of the analysis.

At ten hours all the TiO_2 mixes have formed slightly more cristobalite than the standard mix, with the exception of the five per cent mix which is about five percent less than the standard mix. At 20 hours the cristobalite phase increased in all mixes and at 30 hours had decreased with the exception of the three percent TiO_2 mix which had increased. At 40 hours the cristobalite is still increasing in the standard mix but has decreased in the mixes containing the TiO_2 . The 1, 2, and 3 percent TiO_2 mixes have approximately the same amount of the cristobalite phase present, the 4 and 5 percent mixes have considerably less cristobalite present, the 5 percent TiO_2 mix being approximately 14% less than the standard mix.

From the study and comparison of the first two graphs it is found that in almost all cases upon addition of TiO_2 the quartz and cristobalite phases decrease. Therefore,

the tridymite and glass phase should appear to increase. Graph No. 3 shows this increase. However, since the tridymite was not measured by analysis but obtained by difference between the sum of the quartz and cristobalite phases taken from 100 per cent, the graph represents only a mathematical determination and is subject to the cumulative errors in the determination of quartz and cristobalite.

Taking the major constituents of the standard batch, the amount of liquid present at 1400°C can be calculated from the phase rule diagram, for $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$. Allowing for the impurities in the silica used the percent of the above constituents in the standard mix are CaO 3.35%, Al_2O_3 1.05% and SiO_2 95.6%. The amount of liquid formed at 1400°C is approximately 12.5%. There is no four component phase diagram published for the system $\text{TiO}_2\text{-CaO-SiO}_2$ and Al_2O_3 . However from a study of the phase rule diagrams for $\text{SiO}_2\text{-TiO}_2$, $\text{TiO}_2\text{-Al}_2\text{O}_3$, $\text{CaO-TiO}_2\text{-TiO}_2$ and the system $\text{CaO-SiO}_2\text{-CaO-SiO}_2\text{-TiO}_2\text{-CaO-Al}_2\text{O}_3\text{-SiO}_2$, it is observed that only a small increase in the amount of liquid will result in additions of TiO_2 up to five percent at 1400°C .

The tridymite phase increases about 6% when one and two percent of TiO_2 is added, and approximately 14% when 5 percent TiO_2 is added. If the amount of TiO_2 added is subtracted in each case then for additions up to one and two percent the increase is approximately 6% in the tridy-

mite phase. For additions of 4 or 5% TiO_2 the increase is approximately 12 percent.

When three percent titanium is added to the standard mix the amount of quartz present in the fired samples is equal (within two percent on the sample fired for ten hours) or is greater than the amount of quartz present in the samples of the standard mix. In all cases it is greater than for the mixes containing 1, 2, 4 or 5 percent titanium dioxide.

The samples fired for 30 and 40 hours containing three percent titanium dioxide have approximately five percent more quartz than the samples of the standard mix. With the limited data available no definite conclusion or explanation of the phenomena can be drawn or given.

Conclusions:

From the data and results obtained in the $1400^{\circ}C$ firing of the various silica brick batch compositions there is definite evidence of the increased conversion due to the titanium dioxide present in the mix. The increased conversion appears as the tridymite phase in the fired silica brick. Additions of one and two percent titanium dioxide give an increase of approximately six percent in the tridymite phase.

When three percent titanium dioxide is added a

reaction occurs which tends to limit the conversion to tridymite. The data available is too limited for any explanation of this phenomena to be offered.

SUMMARY

1. A method of standardizing the Norelco X-ray Diffraction Spectrometer and of obtaining quantitative analysis by measuring the area under the maximum diffraction peaks using the mechanical impulse counter is given. Results obtained using this method are presented. For the type of study involved in this investigation, this method is believed to be the most accurate and less time consuming than other methods in use at the present time.

2. Using the standardization procedure for the x-ray machine, a procedure was developed for studying the reactions of silica at high temperatures, using an x-ray furnace designed and built for the Norelco X-ray Diffraction Spectrometer.

3. The effect of the addition of titanium dioxide to silica brick was studied by quantitative analysis x-ray methods on the fired samples and the conclusion drawn that titanium dioxide added to the silica brick batch does increase the rate of conversion of the quartz to tridymite. It is believed that the increase in thermal shock and spalling resistance as noted by Hugill and Rees is due to a large extent to the increase in the tridymite phase.

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