THE

APPROACH TO EQUILIBRIUM

OF

MIXTURES OF CaO, Al_2O_3, AND SiO_2
HEATED TO VARIOUS TEMPERATURES

by

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I. INTRODUCTION AND LITERATURE REVIEW

Whether equilibrium is attained by ceramic materials in ordinary ceramic processes has been a controversial question for many years. The literature indicates, with few exceptions, that equilibrium is never closely approached by ceramic products with the exception of glasses. As far back as 1907, Mellor,[1] as quoted by Foster,[2] says, "The chemistry of pottery is largely a chemistry of incomplete reactions." Foster goes on to say that Mellor's law of non-equilibrium of ceramic bodies, as he calls it, has become one of the accepted fundamental laws of ceramics.

Foster himself admits that in many cases there is no question of the validity of Mellor's law. There is a tendency today, however, toward finer grinding, more intimate mixing, using of purer commercial materials, and firing to higher temperatures. Any one of these changes would greatly enhance the chances of attaining equilibrium in ceramic products as predicted from the equilibrium phase diagrams. If ceramic products would closely approach equilibrium, the phase diagrams would be powerful tools in the development of ceramic bodies. The American Ceramic Society, recognizing the importance of the diagrams, made available a large collection compiled by Hall and Insley.[3] Prior to this, Sosman and Anderson had made available enlarged,

revised diagrams of the refractory oxides. It was on Plate II of these diagrams that the calculations for this work were based.

Riddle[5] in delivering the Edward Orton Junior Fellow Lecture before the American Ceramic Society pointed out that the significance of the subsidiary or enclosed triangle (composition, solidus, or compatibility triangle) is probably not fully appreciated. He further said that the crystalline phases which will be formed in a ceramic product can be easily predicted by determining which compounds form the apices of the triangle within which the composition of the ceramic product falls. It is gratifying, he continues, to know that spark plug porcelains show a close approach to equilibrium.

Foster and Royal[6] in their study of the binary system $BeO \cdot Al_2O_3 - Al_2O_3$ found that the reactions of their mixtures made from pure oxides were 98 percent complete after calcination to cone 35.

Morgan and Hummel[7] working with mixtures of BeO and SiO_2 found that they could not synthesize phenacite $(2BeO \cdot SiO_2)$ from the pure oxides by firing to $1500°$ C. Upon the addition of as little as 0.2 percent willemite $(ZnO \cdot SiO_2)$, however, the X-ray patterns revealed the presence of phenacite as the only phase present at a

temperature of 1500° C. with a five hour hold. The samples showed no sign of distortion.

In connection with the addition of mineralizers to ceramic mixtures, Bowen[8] in a discussion of solidus triangles said that when moderate amounts of fluxes such as feldspar are added, no major changes are likely in the relations of the equilibrium phases except of course in the formation of glass at lower temperatures or an increase in the amount of glass at any given temperature.

In direct contrast to the above statement, Hall and Insley[3] said that the presence of an impurity even in small amounts introduces an additional component which in many instances alters the solubility and melting relations so profoundly that no adequate interpretation on the basis of the simpler diagram is possible.

Goldsmith and Ehlers[9] in a paper describing the stability relations of anorthite found that this mineral can be formed from the oxides at a temperature as low as 350° C.

Yoder[10] working with compositions in the anorthite-wollastonite-gehlenite composition triangle of the $CaO-Al_2O_3-SiO_2$ ternary system succeeded in forming these minerals from quartz, beta alumina, and calcite and from kaolin, quartz, and calcite at temperatures as low as 900° C. after an extended holding period.

Foster,[11] studying the stability relations of synthetic
sapphirine in the $MgO-Al_2O_3-SiO_2$ ternary system, discovered
that the reactions in his compositions were remarkably com-
plete after one calcination at 1450° C. in the presence of
little or no liquid.

The above papers seem to indicate that solid state
reactions in ceramic bodies play a very prominent part in
the attainment of equilibrium.

The $CaO-Al_2O_3-SiO_2$ system was the first ternary sys-
tem completely studied by the Geophysical Laboratory of the
Carnegie Institution of Washington. Since Rankin and Wright[12]
published their phase diagram in 1915, it has been of great
use in the fields of metallurgical slags and hydraulic ce-
ments. This investigation was concerned with only a small
portion of the high alumina end of this diagram, specifically
compositions within the anorthite-mullite-cristobalite and
the anorthite-gehlenite-corundum compatibility triangles.

Foster[2] points out that a great contributing factor to
the identification of fine grained crystalline phases in
ceramic bodies is the more general application of X-ray
diffraction techniques. For many years, the petrographic
microscope was the chief means of identifying crystals in
ceramic products. In many cases, especially in reactions
that take place almost entirely in the solid state, the
crystalline phases are too minute to be distinguished by

the microscope and only X-ray diffraction methods can be used to identify the crystals. It has been through this improved method of identification that the possibility of closely approaching equilibrium in the solid state is gradually becoming recognized.

Quantitative analysis by means of a geiger-counter X-ray spectrometer has been done quite often in the ceramic field. Tuttle and Cook[13] compared X-ray photographic procedures with the spectrometer method and found that the spectrometer method was much less time consuming and just as accurate. They determined quantitatively the crystalline phases present in blends of feldspar, clay, and flint with considerable success by measuring the height and width of the intensity peaks above the background.

Duwez and Odell[14] used the geiger-counter spectrometer for the quantitative determination of different crystallographic forms of zirconia. They used the rotating specimen method and claimed an accuracy of ± 6 percent. In a discussion of this paper, R. A. Hatch of the Bureau of Mines suggested a method of mounting the specimens recommended to him by John Abbott of the North American Philipps Company which would reduce preferred orientation of the crystals. This method was used exclusively in this experiment.

Sane and Cook[15] determined the amounts of quartz and mullite in several whiteware bodies by measuring the height

of the intensity peaks above the background.

II. PURPOSE OF INVESTIGATION

Equilibrium conditions in the $CaO-Al_2O_3-SiO_2$ ternary system as shown by the equilibrium diagram were established by allowing the solid phases to crystallize out of a liquid phase at specific temperatures. The purpose of this investigation was to determine whether equilibrium was attained or was closely approached when certain compositions of the anorthite-mullite-cristobalite and the anorthite-gehlenite-corundum compatibility triangles were fired to 1400° C. The effect on equilibrium of different raw materials used to form the compositions was also studied.

III. PLAN OF INVESTIGATION

(1) Eight compositions were studied, four in the anorthite-mullite-cristobalite triangle and four in the anorthite-gehlenite-corundum triangle. All the compositions were in the primary field of corundum and according to the phase diagram only 10 percent liquid phase would be formed at 1400° C.

(2) Bulk density, absorption, and modulus of rupture were

determined on samples made from different end members after they were fired to 1400° C. and held at this temperature for twelve hours. Absorption and bulk density were also determined on specimens prepared from the oxide end members after firing to 1130° C., 1170° C., and 1350° C.

(3) Samples made from the oxides were withdrawn from the kiln at 20° C. intervals between 1200° C. and 1400° C. with no soaking period and also withdrawn at 1400° C. with various lengths of soaking periods. The samples were quenched in air. It was hoped that by this means it would be possible to study the crystallization path or reactions of the compositions.

(4) X-ray diffraction patterns were made of all the specimens to determine the reaction products formed during heat treatment. Qualitative and quantitative interpretations were made from the X-ray patterns.

The method employed in the quantitative analysis of the X-ray patterns was chosen because of its speed and simplicity. It was accomplished by measuring the height of a specific intensity peak of a mineral and determining the percent of that material in the specimen from a calibration curve constructed from known percentages of the mineral. It is recognized that more precise methods

can be used. The writer feels, however, that because of the high degree of reproducibility observed with repeated trials the method was accurate at least to ± 5 percent.

(5) The petrographic microscope was used to determine crystal and glass phases whenever possible. Its greatest value was to determine whether any glass was present and also to determine whether the crystals were formed by solid state reactions or by crystallization from the liquid phase.

IV. MATERIALS

The raw materials used in this investigation were silica, alumina, calcium carbonate, and kaolin. In addition anorthite, gehlenite, and mullite synthesized in the laboratory were used. The mullite used to construct the calibration curves for the quantitative analysis by means of the X-ray was electric furnace mullite made at the plant of the Babcock and Wilcox Company in Augusta, Georgia.

The silica was commercial potter's flint supplied by the Pennsylvania Pulverizing Company, of Lewiston, Pennsylvania. It was ground to a fineness of 99 percent through a 200 mesh screen.

Commercial alumina, A-2 grade, ground to pass through a 325 mesh screen was the source of corundum. This

material was supplied by the Aluminum Ore Company of East Saint Louis, Illinois.

The kaolin used was Pioneer Georgia Kaolin, a product of the Georgia Kaolin Company, of Elizabeth, New Jersey. This material is a washed, air-floated grade used extensively throughout the ceramic industry.

C. P. calcium carbonate, molecular weight 100.09, was used in all mixtures.

Synthesized Minerals

Alumina, silica, and calcium carbonate were mixed in the proper molar proportions to form $CaO \cdot Al_2O_3 \cdot 2SiO_2$, $2CaO \cdot Al_2O_3 \cdot SiO_2$, and $3Al_2O_3 \cdot 2SiO_2$. The mixtures were placed in distilled water and thoroughly stirred to promote very intimate mixing of the components. After the mixtures were dried, they were pressed into bars $4" \times \frac{1}{2}" \times \frac{1}{2}"$ and fired to 1500° C. and allowed to remain at this temperature for 24 hours. After cooling, the bars were ground to pass through a 200 mesh screen.

X-ray patterns of the synthesized anorthite and gehlenite disclosed that the mixtures were completely converted to the pure compounds. No phases other than the anorthite and gehlenite were seen. This was confirmed by the petrographic microscope, which revealed no sign of any unreacted material.

The mullite mixture when analyzed by means of the X ray and the petrographic microscope showed the reaction to be far from complete. It was actually a mixture of mullite and unreacted corundum and cristobalite. It was decided, however, to use this mixture without subjecting it to any more heat treatment since the composition was essentially that of pure mullite. It was therefore added to the compositions as if it were 100 percent mullite.

The chemical analysis of the raw materials and the oxide constituents of the synthesized minerals are given in table 1.

V. METHOD OF INVESTIGATION

Location of compositions studied

Figure 1 shows the positions of the eight compositions studied in the $CaO-Al_2O_3-SiO_2$ ternary system. The compositions in the anorthite-mullite-cristobalite compatibility triangle were located so that at 1400° C. each composition under equilibrium conditions would have 10 percent liquid phase of composition A, and the compositions in the anorthite-gehlenite-corundum compatibility triangle at 1400° C. would have 10 percent liquid phase of composition B at equilibrium. All the compositions were located in the primary field of corundum.

The compositions expressed as percentages by weight of the oxides are shown in table 2.

Calculation of the mixtures

The silica, alumina, and calcium carbonate were regarded as being 100 percent pure for calculating the composition of the mixtures. In the mixture containing kaolin all of the silica and part of the alumina requirements were supplied by this material. Only the alumina and silica reported in the chemical analysis of the kaolin was calculated into the batches. The other oxides were allowed to go along as so much excess. Three groups of mixtures of each composition were prepared using different end members. The compositions expressed as percentages by weight of the raw materials are shown in tables 3, 4, and 5.

The materials were individually weighed to the closest hundredth of a gram on a laboratory pharmaceutical balance having a capacity of 120 grams.

Each mixture was placed in a cylindrical metal container and the container was placed in turn on a ball mill rack so that the long axis of the cylinder was perpendicular to the axis of rotation. The tumbling action which ensued effected thorough mixing of the constituents. Each mixture was rotated for one hour.

Preparation of the samples

The specimens were pressed in the form of circular disks 1" in diameter and bars 4" x ½" x ½". Approximately 8 grams of material were used for the disks and 35 grams for the bars. Both the bars and the disks were pressed on a Denison Hydraulic Press under a load of 4000 pounds. A small amount of distilled water was used to bond and mixtures. Some of the bars composed of the oxide end members were cut in thirds for use in studying crystallization progress at intermediate temperatures. No bars were made for the compositions prepared from the synthetic minerals.

Firing of the samples

All the samples were fired in a Pereny electric furnace made by the Pereny Equipment Company of Columbus, Ohio, heated by silicon carbide elements. The temperature was measured by means of platinum, platinum-13 percent rhodium thermocouple placed in the immediate vicinity of the samples and connected to a Leeds and Northrup portable potentiometer with an accuracy of $\pm 2^{\circ}$ C. Throughout the investigation the kiln was set so that the temperature rise was approximately 100 $^{\circ}$ C. per hour.

Five disks and five bars of each of the eight compositions were fired to 1400 $^{\circ}$ C. and held at this temperature for twelve hours. Five disks of each composition of the

group prepared from the oxides were also fired to 1130° C., 1170° C., and 1350° C. and held for twelve hours at each temperature. The disks were used to determine bulk density and absorption and the bars were used to determine modulus of rupture.

The bars cut in thirds were withdrawn from the kiln at 20° C. intervals between 1200° C. and 1400° C. with no holding period and also at 1400° C. with soaking periods of 3/4, 1½, 3, 6, and 12 hours. One sample of each composition was allowed to cool with the furnace after the twelve hour soak. The samples withdrawn from the kiln were quenched in air.

In addition to the samples described above, the eutectic composition in the wollastonite-gehlenite-anorthite compatibility triangle having an oxide analysis of 38.0 percent CaO, 20.0 percent Al_2O_3, and 42.0 percent SiO_2 was prepared from alumina, silica, and calcium carbonate. This mixtrue, which melts at 1266° C., was pressed into bars as described and fired to 1250° C. with a 24 hour soaking period. The bars were ground to pass through a 200 mesh screen and mixed with corundum and quartz in the proper proportions to form composition number 7. This mixture was pressed into disks and fired to 1400° C. Disks were withdrawn from the kiln and quenched in air at 1270° C., 1300° C., 1350° C., and 1400° C. with no holding period. Specimens were also

removed and quenched at 140° C. with various soaking periods up to twelve hours. The remaining samples were allowed to cool down with the furnace after the twelve hour holding period.

Throughout the investigation additional samples of all the groups were fired to various temperatures whenever it was deemed necessary to clarify or substantiate some of the results obtained.

Testing methods

Absorption and density were determined from the disks by the prescribed A. S. T. M. methods for electrical porcelains. The modulus of rupture of the bars was determined, using a Tinius Olsen laboratory testing machine.

A General Electric KRD-3 X-ray unit equipped with a geiger-counter spectrometer was used for the determination of the crystal phases present in the specimens. All of the material was ground to pass a 325 mesh screen before being X-rayed. The sample holder was a rectangular piece of aluminum 2" x 1" x 1/16" with a 1" x 9/16" rectangular hole cut completely through it. The sample holder was placed over a glass slide and the material to be X-rayed was poured onto the portion of the slide left exposed by the holder. The material was pressed down firmly with a thin spatula and the excess struck off. A second glass slide was placed

over the aluminum holder in the machine. The first glass
slide was then removed and the untouched surface of the
packed sample was exposed to the X-ray beam. This method
of mounting the samples was used in order to minimize pre-
ferred orientation of the crystals. Each specimen was
scanned through values of 2 θ from 15 to 70 degrees using
a copper target at a speed of 2 degrees per minute. The
width of the beam was one degree and the target angle was
4 degrees.

Standard mixtures of varying known percentages of anor-
thite with corundum, anorthite with mullite, corundum with
cristobalite and quartz, and mullite with cristobalite and
quartz were prepared and X-rayed in order to construct cali-
bration curves for a quantitative analysis of the specimens.
Electric furnace mullite, synthesized anorthite, A-2 corun-
dum, and calcined quartz were the materials used in the
standard mixtures. The values of 2 θ measured were 26.0°
for mullite, 27.8° for anorthite, 57.5° and 68.1° for corun-
dum, and 21.8° for cristobalite. Two angles were used for
corundum because at 57.5° mullite and corundum peaks coincide
and it was not possible to measure accurately the residual
corundum in compositions 1 through 4. The curves were con-
structed by measuring the height of the peaks above the
background and dividing by the geight of the peak for the
respective material at 100 percent. This value was plotted

against the known percentage of the material. In this way
it was possible to plot two curves for each mineral. For
instance, a calibration curve was plotted for mullite when
mixed with anorthite and also when it was mixed with calcined
quartz. The effect on the intensity of a given peak for one
material when it was combined with different materials could
then be evaluated and would give an indication of the relia-
bility of the calibration. Upon comparison, the two curves
of the same mineral combined with different materials proved
to be practically identical.

The calcined quartz was a mixtrue of quartz and cristo-
balite; therefore only relative values of the height of the
intensity peak at different percentages of cristobalite
could be obtained. Since no cristobalite was found in the
X-ray patterns that were analyzed, no calibration curve was
constructed for this mineral.

Each point on each curve was the average of three sepa-
rate measurements of the intensity peaks of the standard
mixture. The General Electric XRD-3 unit records the in-
tensity logarithmically and it was necessary to convert each
peak to linear measurements.

VI. SAMPLE CALCULATIONS

The numerical values for the calibration curves were obtained from the following formula:

$$\frac{H}{H\text{-}100o/o} = X$$

where,

H = the height above the background of a intensity peak at a specific value of 2 θ for a mineral when a known percentage of the mineral is present.

H-100o/o= the height above the background of the intensity peak at the same value of 2 θ for the same mineral when 100 o/o of the mineral is present.

Analysis of X-ray Patterns
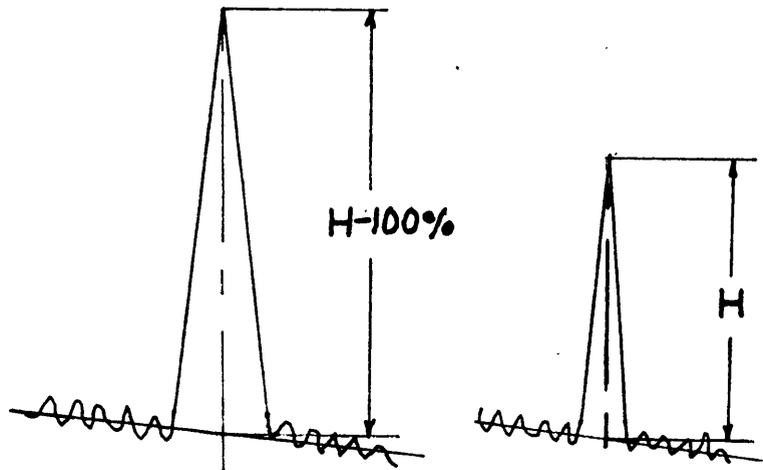
Example

For a mixture containing 80 o/o corundum the value of X for the intensity peak at 57.5° was:

> H-100 0/o for.corundum at 57.5° = 970
>
> H for 80 o/o corundum at 57.5° = 670
>
> therefore $\frac{670}{970}$ = 0.69

All the values of the calibration curves for various percentages of mullite, anorthite, and cristobalite were obtained in the same manner.

For a specimen containing an unknown amount of a mineral the value of H was measured, divided by H-100 o/o and the percentage of the mineral in the specimen was read from the graph.

VII. DATA AND RESULTS

Plates 1 to 3 are X-ray patterns of the raw materials used in the investigation.

Plates 4-11 are X-ray patterns of the specimens prepared from the different raw materials as shown in tables 3, 4, and 5 after they were fired to 1400° C., held at this temperature for 12 hours, and allowed to cool slowly with the furnace.

Figure 1

Diagram of CaO-Al₂O₃-SiO₂ System

Showing Locations of Compositions

Diagram of CaO-Al$_2$O$_3$-SiO$_2$ System Showing Locations of Compositions

GEORGIA PIONEER KAOLIN

65   60   55   50   45   40   35   30   25   20

GEORGIA PIONEER KAOLIN
1400°C

65   60   55   50   45   40   35   30   25   20

A-2 ALUMINA

65   60   55   50   45   40   35   30   25   20

PLATE 1

Synthetic Anorthite

65 60 55 50 45 40 30 30 25 20

Electric Furnace Mullite

66 61 56 51 46 41 36 31 26 21 16

Synthetic Mullite

65 60 55 50 45 40 35 30 25 20

PLATE 2

Synthetic Gehlenite

Pennsylvania Flint

PLATE 3

Composition 1
Oxides

66 61 56 51 46 41 36 31 26 21 16

Composition 1
Synthetic Minerals

67 62 57 52 47 42 37 32 27 22 17

Composition 1
Kaolin

67 62 57 52 47 42 37 32 27 22 17

PLATE 4

Composition 2
Oxides

Composition 2
Synthetic Minerals

Composition 2
Kaolin

PLATE 5

Composition 3
Oxides

66   61   56   51   46   41   36   31   26   21   16

Composition 3
Synthetic Minerals

65   60   55   50   45   40   35   30   25   20

Composition 3
Kaolin

67   62   57   52   47   42   37   32   27   22   17

PLATE 6

Composition 4
Oxides

Composition 4
Synthetic Minerals

Composition 4
Kaolin

PLATE 7

Composition 5
Oxides

Composition 5
Synthetic Minerals

Composition 5
Kaolin

PLATE 8

Composition 6
Oxides

68   63   58   53   48   43   38   33   28   23   18

Composition 6
Synthetic Minerals

65   60   55   50   45   40   35   30   25   20

Composition 6
Kaolin

67   62   57   52   47   42   37   32   27   22   17

PLATE 9

Composition 7

Oxides

66   61   56   51   46   41   36   31   26   21   16

Composition 7

Synthetic Minerals

65   60   55   50   45   40   35   30   25   20

Composition 7

Kaolin

65   60   55   50   45   40   35   30   25   20

PLATE 10

Composition 8
Oxides

Composition 8
Synthetic Minerals

Composition 8
Kaolin

PLATE 11

Eutectic Composition Mixed With
Alumina and Silica To Form Composition 7
1400°C - 12 Hour Hold
Quenched

65   60   55   50   45   40   35   30   25   20
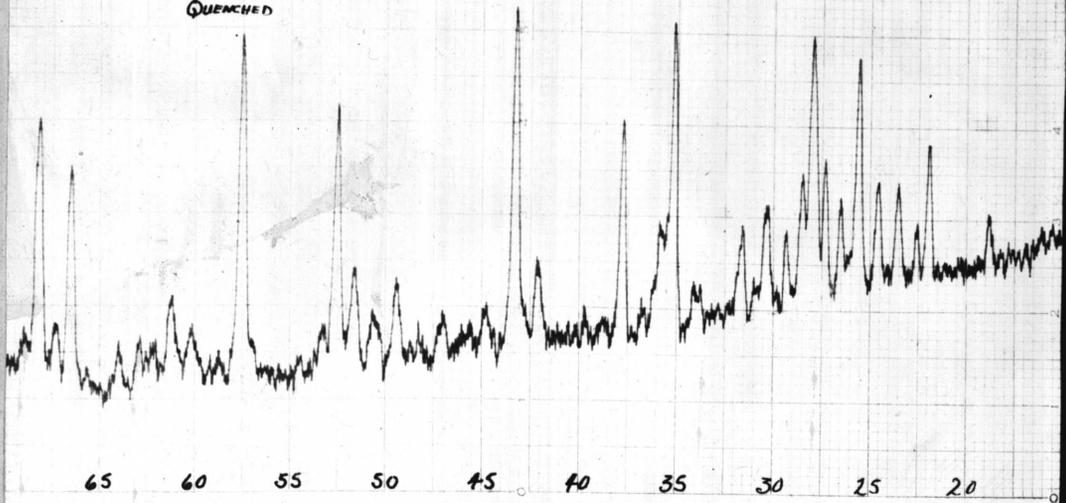
Eutectic
Composition Mixed With
Alumina and Silica To Form Composition 7
1270°C - No Hold
Quenched

66   61   56   51   46   41   36   31   26   21   16
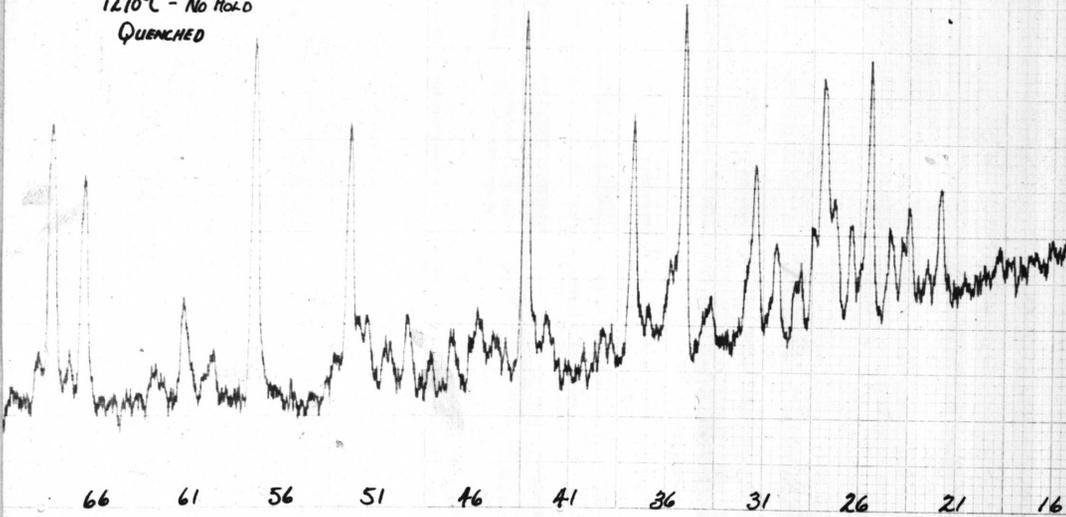
1266°C Eutectic Composition
1250°C - 24 Hour Hold

67   62   57   52   47   42   37   32   27   22   17

PLATE 12

Composition 8
Oxides
1400°C - 12 Hour Hold
Quenched

65 60 55 50 45 40 35 30 25 20

Composition 8
Oxides
1400°C - ¾ Hour Hold
Quenched

65 60 55 50 45 40 35 30 25 20

Composition 8
Oxides
1400°C - No Hold
Quenched

66 61 56 51 46 41 36 31 26 21 16

PLATE 13
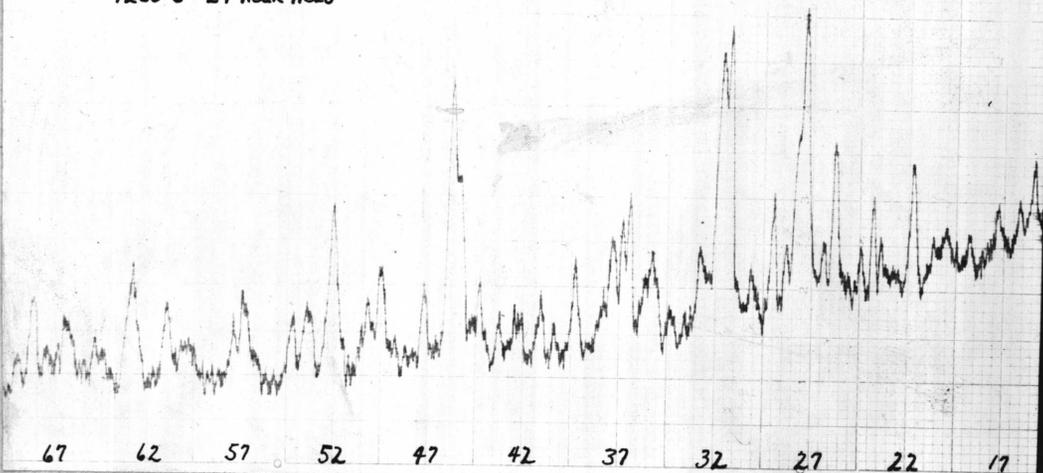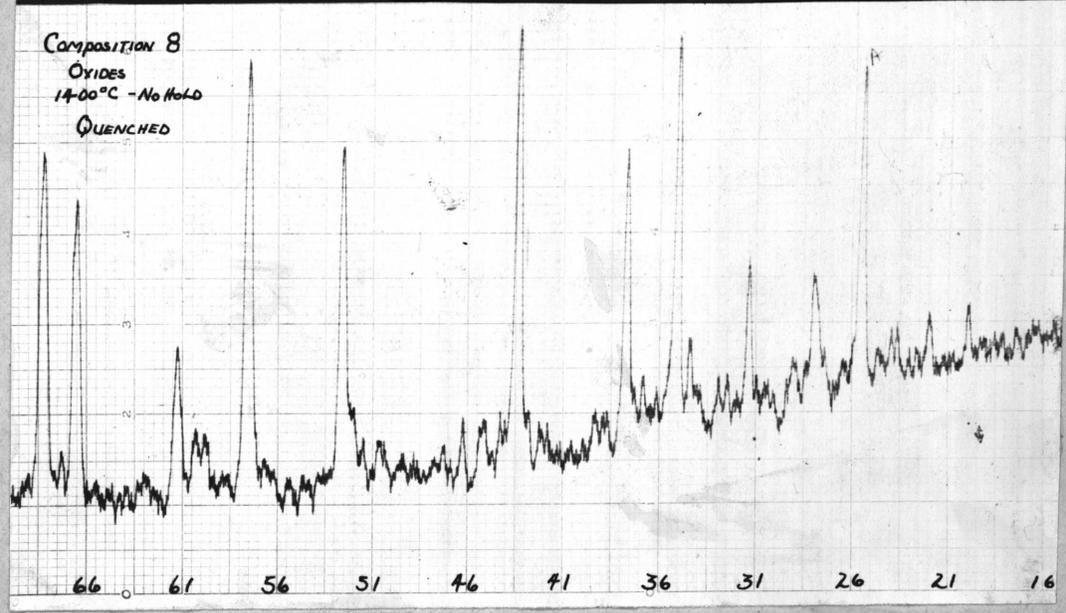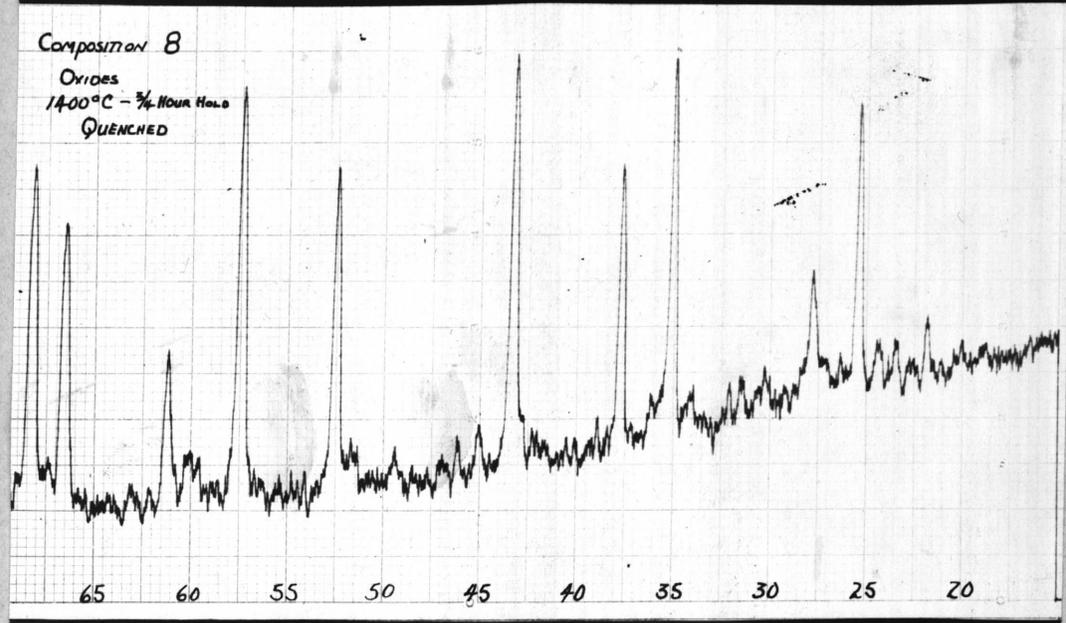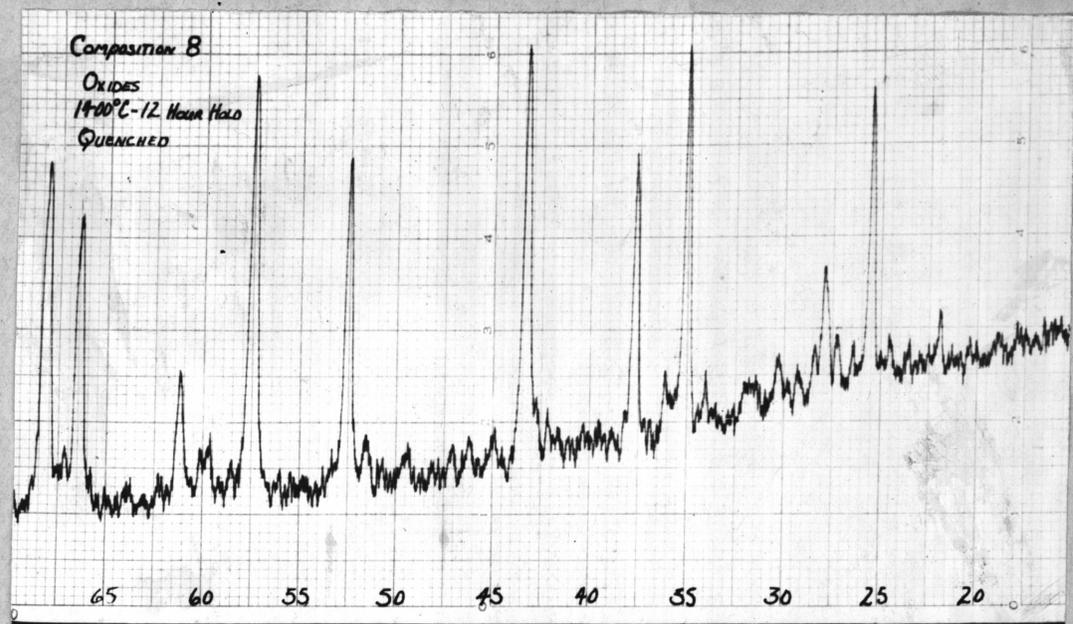
Composition 3
Oxides
1400°C – 6 Hour Hold
Quenched

67 62 57 52 47 42 37 32 27 22 17
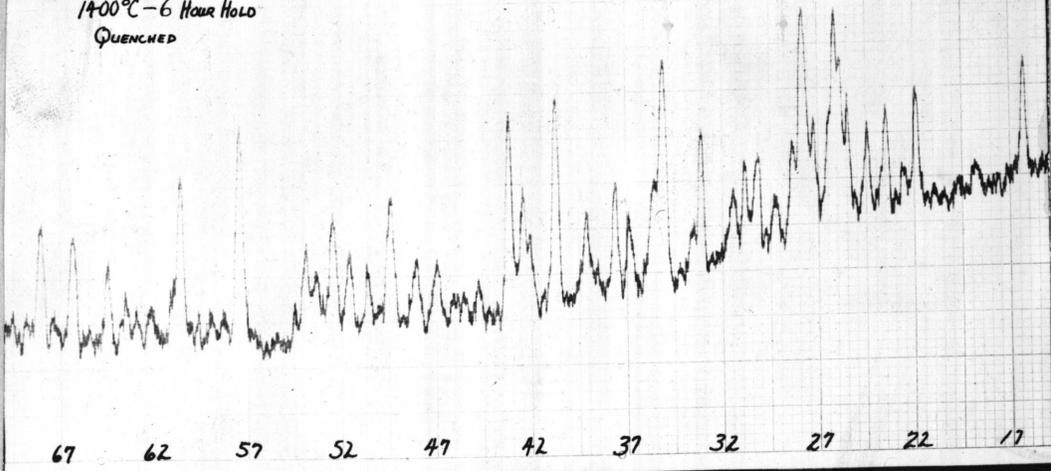
Composition 3
Oxides
1400°C – 3 Hour Hold
Quenched

65 60 55 50 45 40 35 30 25 20
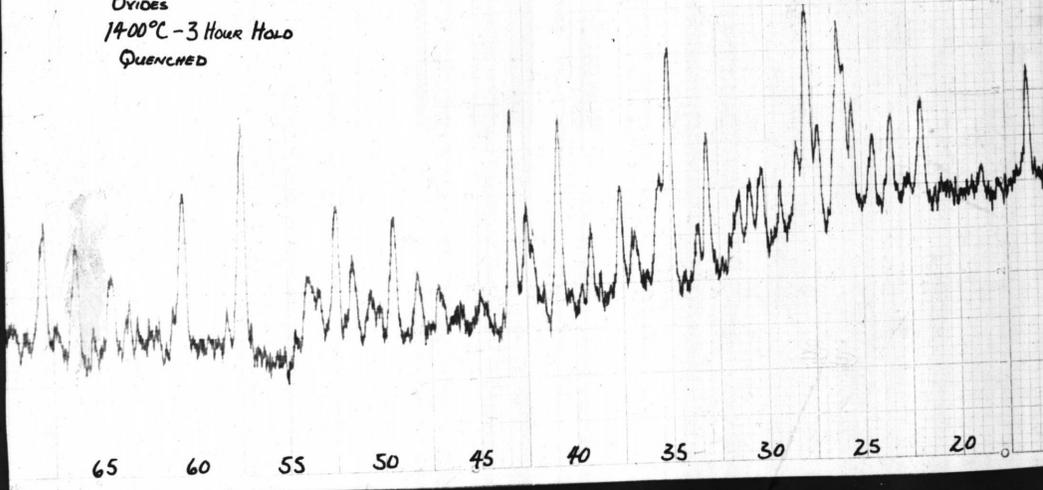
Composition 3
Oxides
1400°C – No Hold
Quenched

66 61 56 51 46 41 36 31 26 21 16

PLATE 14
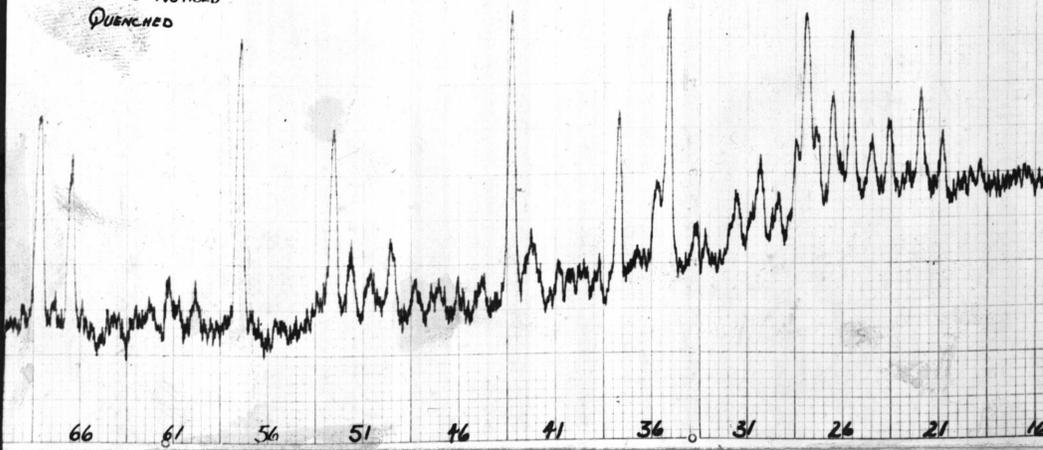
Table 1

Chemical Analysis of the Raw Materials

	A-2 Alumina	Penn. Flint	Pioneer Kaolin	Mullite	Anorthite	Gehlenite
SiO_2	0.02 %	99.820 %	45.34 %	28.2 %	43.3 %	22.0 %
Al_2O_3	99.09	0.121	37.29	71.8	36.6	37.2
MgO		0.006	0.22			
Fe_2O_3	0.04	0.013	0.61			
CaO		0.012	0.25		20.1	40.8
Na_2O	0.55		0.35			
K_2O						
TiO_2	0.002		1.54			
Ign. Loss			14.39			

Table 2

Percent by Weight of the Oxides of Each Composition

Composition No.	CaO	SiO_2	Al_2O_3
1	16.0	43.0	41.0
2	12.0	40.0	48.0
3	8.0	37.0	55.0
4	4.0	34.0	62.0
5	19.0	38.0	43.0
6	14.0	27.0	59.0
7	10.0	19.0	71.0
8	5.0	8.0	87.0
A	11.3	24.1	64.6
B	28.1	39.5	32.4

Table 3

Group 1--Oxides

Percent by Weight of Raw Materials

Composition No.	Penn. Flint	A-2 Alumina	Calcium Carbonate
1	38.20	36.42	25.38
2	36.55	43.86	19.58
3	34.81	51.75	13.44
4	32.96	60.11	6.92
5	33.06	37.41	29.52
6	24.32	53.15	22.52
7	17.62	65.82	16.56
8	7.70	83.71	8.59

Table 4

Group 2--Kaolin

Percent by Weight of Raw Materials

Composition No.	Kaolin	A-2 Alumina	Calcium Carbonate
1	70.54	4.08	25.38
2	67.51	12.91	19.58
3	64.29	22.27	13.44
4	60.88	32.20	6.92
5	61.06	9.42	29.52
6	44.92	32.56	22.52
7	32.53	50.91	16.56
8	14.20	77.21	8.59

Table 5

Group 3--Synthetic Materials

Percent by Weight of Raw Materials

Composition No.	Penn. Flint	Mullite	Anorthite	Gehlenite	A-2 Alumina
1	3.7	16.5	79.8		
2	3.9	36.3	59.8		
3	3.9	56.2	39.9		
4	3.8	76.1	20.1		
5			85.5	4.5	10.0
6			59.8	5.0	35.2
7			41.7	4.0	54.3
8			16.2	4.3	79.5

Table 6

Data for Calibration Curves

Prepared Mixtures		$\dfrac{H}{H-100\%}$	
Mullite (%)	Anorthite (%)	Mullite	Anorthite
0	100	—	1.00
10	90	0.05	0.94
20	80	0.12	0.86
40	60	0.26	0.73
60	40	0.46	0.52
80	20	0.68	0.27
100	0	1.00	—

Table 7

Data for Calibration Curves

Prepared Mixtures		$\dfrac{H}{H\text{-}100\%}$	
Mullite (%)	*Cristobalite (%)	Mullite	*Cristobalite
0	100	—	1.00
10	90	0.05	0.90
20	80	0.12	0.79
40	60	0.28	0.69
60	40	0.42	0.55
80	20	0.68	0.31
100	0	1.00	—

* The calcined quartz was actually a mixture of quartz and cristobalite so all the values shown for cristobalite are relative values.

Table 8

Data for Calibration Curves

Prepared Mixtures		$\frac{H}{H\text{-}100\%}$		
Anorthite (%)	Corundum (%)	Anorthite	Corundum	
			57.5°	68.1°
100	0	1.00	—	—
90	10	0.95	0.04	0.06
80	20	0.88	0.13	0.12
60	40	0.72	0.28	0.27
40	60	0.52	0.50	0.42
20	80	0.29	0.69	0.59
10	90	0.04	0.78	0.68
0	100	—	1.00	1.00

Table 9

Data for Calibration Curves

Prepared Mixtures		$\dfrac{H}{H-100\%}$	
Cristobalite (%)	Corundum (%)	Cristobalite	Corundum
0	100	—	1.00
20	80	0.29	0.69
40	60	0.48	0.50
60	40	0.65	0.32
80	20	0.86	0.13
90	10	0.92	0.04
100	0	1.00	—

Figure 2

Calibration curve for Mullite (2 θ = 26.0°)
Mixed with Cristobalite.
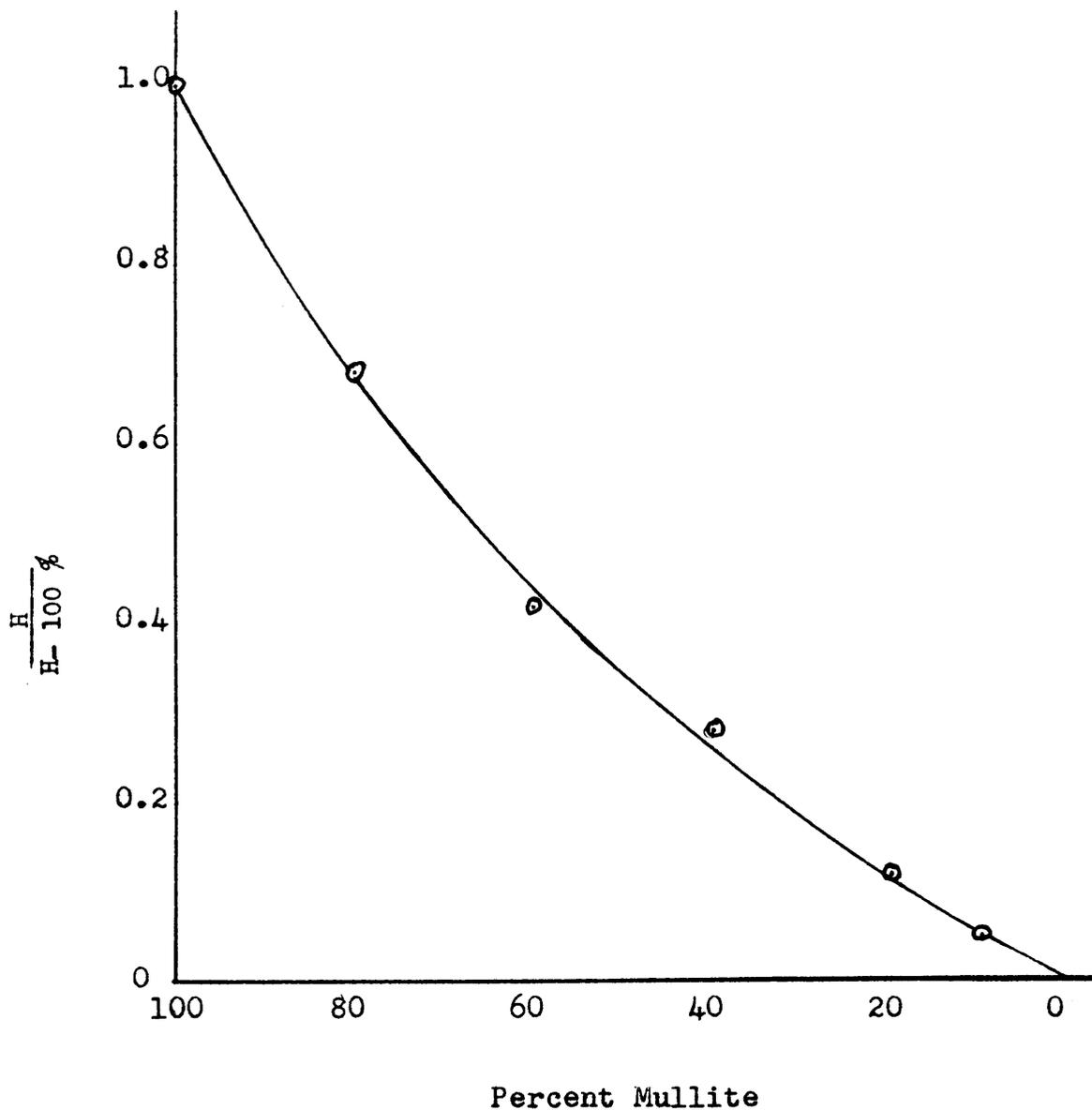
Figure 3

Calibration curve for Mullite (2 θ = 26.0°)
Mixed with Anorthite

Percent Mullite
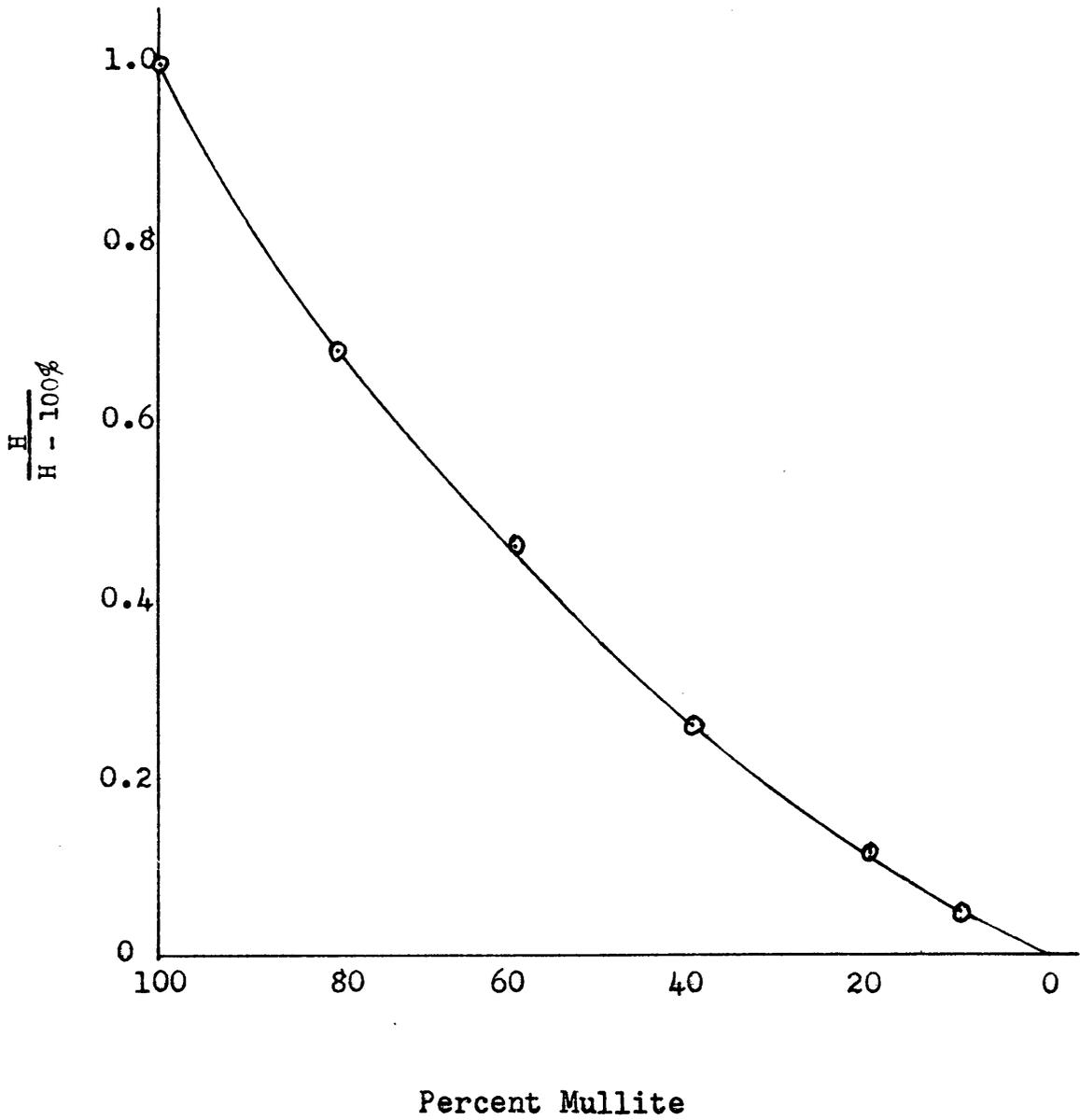
Figure 4

Calibration Curves for Anorthite (2 θ = 27.8°)

Mixed with Alumina and Corundum (2 θ = 57.8°)

Mixed with Anorthite

Percent Anorthite or Corundum
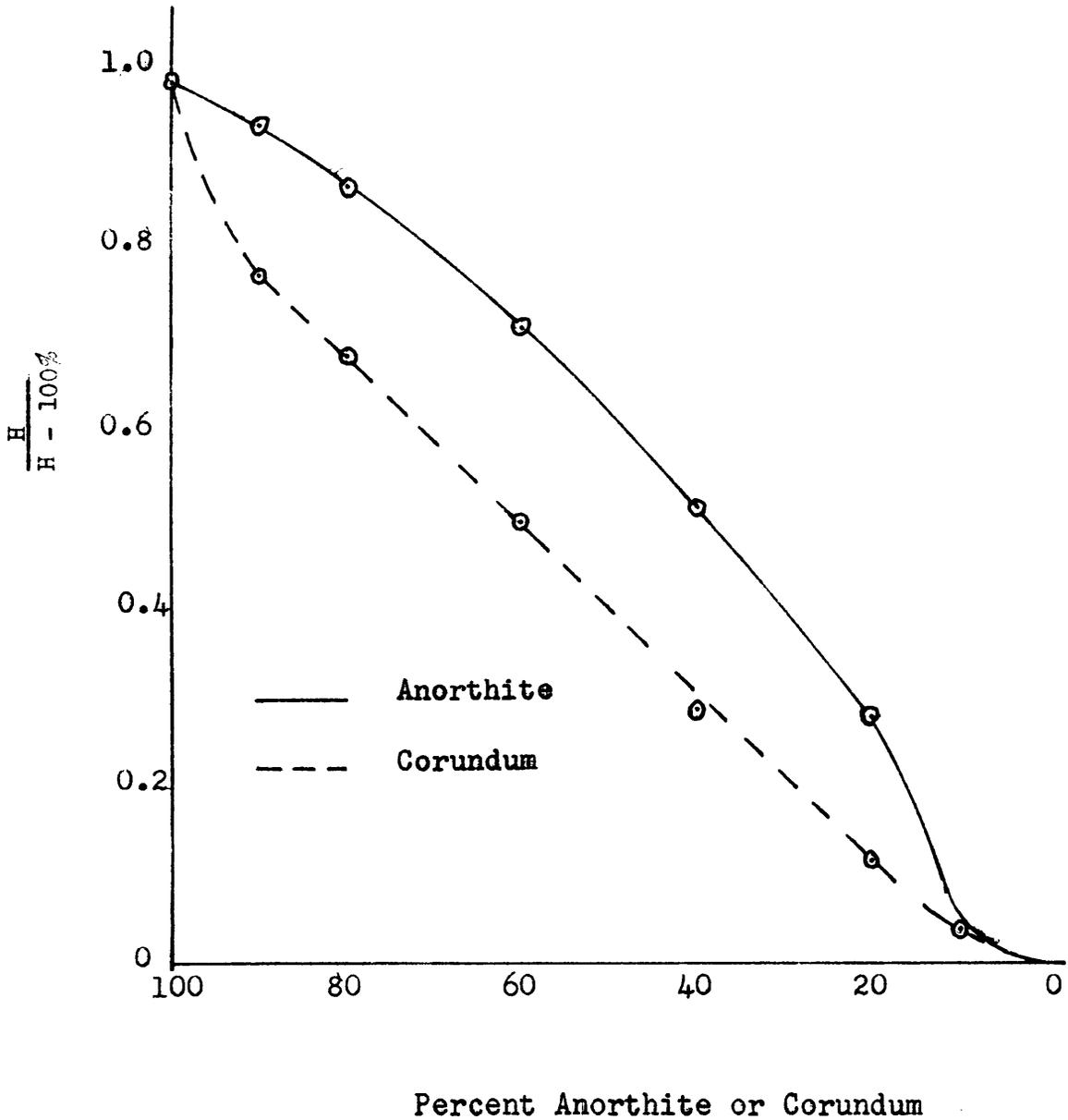
Figure 5

Calibration Curves for Anorthite (2 θ = 27.8°)

Mixed with Mullite and Corundum (2 θ = 57.5°)

Mixed with Cristobalite
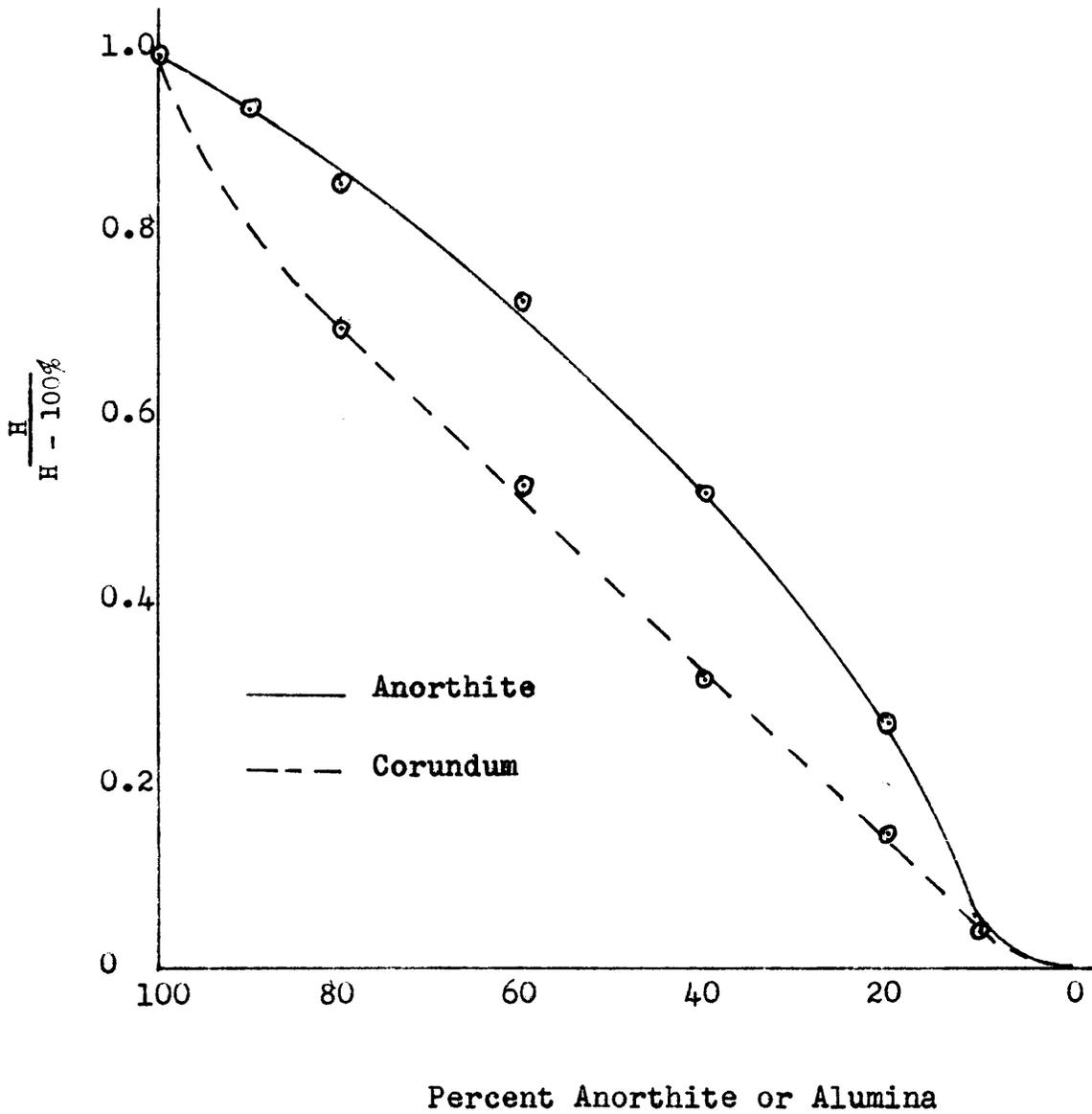
Figure   6

Calibration Curve for Corundum   (2 θ = 68.1°)

Mixed with Anorthite

Percent Alumina
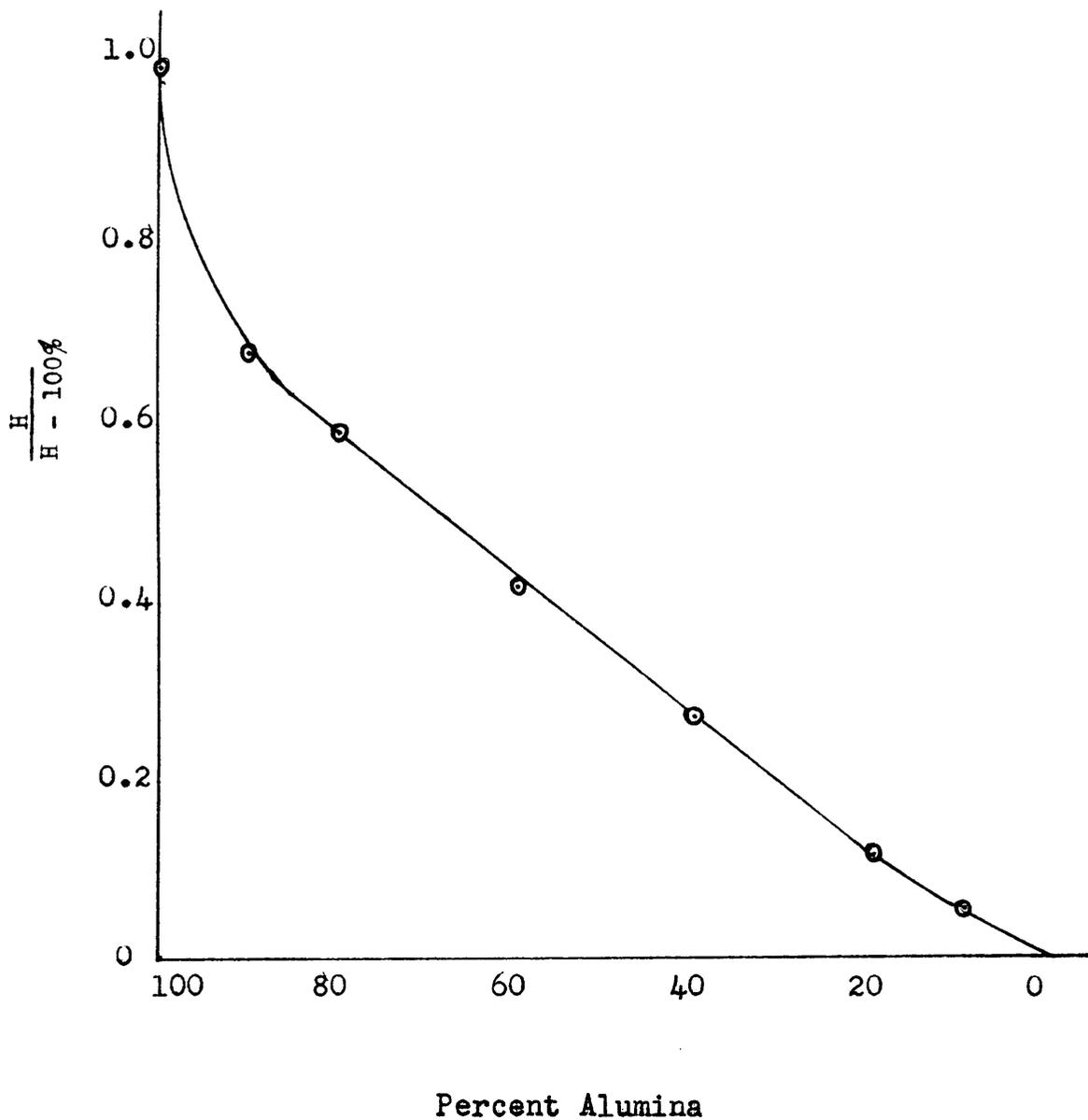
Table 10

Group 1--Oxides

Percent Crystalline Content of Samples Held for 12 Hours at 1400° C. and Allowed to Cool Slowly with the Furnace

Composition No.	Anorthite	Mullite	Residual Corundum	Glass by Difference
1	81	14	4	1
2	59	35	4	2
3	40	50	3	7
4	19	58	7	16

Composition No.	Anorthite	Corundum	Gehlenite*	Glass by Difference
5	83	8	4	2
6	60	36	3	4
7	41	56	2	3
8	16	77	3	5

* Estimated from intensity peaks at 31.4° of known mixtures.

Table 11

Group 2--Kaolin

Percent Crystalline Content of Samples Held for 12 Hours
at 1400° C. and Allowed to Cool Slowly with the Furnace

Composition No.	Anorthite	Mullite	Residual Corundum	Glass by Difference
1	82	11	2	5
2	60	33	2	5
3	42	51	3	4
4	21	69	3	7

Composition No.	Anorthite	Corundum	Gehlenite	Glass by Difference
5	82	8	5	5
6	45	36	12	7
7	30	56	6	8
8	10	77	5	8

Table 12

<u>Group 3--Synthetic Materials</u>

<u>Percent Crystalline Content of Samples Held for 12 Hours at 1400° C. and Allowed to Cool Slowly with the Furnace</u>

Composition No.	Anorthite	Mullite	Residual Corundum	Glass by Difference
1	74	16	1	9
2	56	36	2	6
3	40	55	2	3
4	19	71	7	3

Composition No.	Anorthite	Corundum	Gehlinite	Glass by Difference
5	82	10	4	4
6	46	33	6	15
7	38	46	4	12
8	12	79	4	5

Table 13

Comparison of Percent Crystalline Content of Samples Prepared from

the Oxides, Held for 12 Hours at 1400° C. and Quenched in Air, and the

Percent Minerals Predicted by the Equilibrium Diagram at 1400 °C.

Composition No.	Observed Percent			Predicted Percent		
	Anorthite	Corundum	Glass by Difference	Anorthite	Corundum	Liquid Phase
5	79	10	11	80	10	10
6	58	32	10	55	35	10
7	40	53	7	37	53	10
8	12	79	9	11	79	10

Table 14

Absorption and Density of Samples Prepared from the Oxides
and Fired to Various Temperatures with a 12 Hour Soak

Temperature (°C.)

Composition No.	1130		1170		1350	
	Absorption (%)	Bulk Density (g/cc)	Absorption (%)	Bulk Density (g/cc)	Absorption (%)	Bulk Density (g/cc)
1	34.0	1.47	29.0	1.58	31.0	1.48
2	29.5	1.51	26.9	1.66	27.4	1.60
3	26.0	1.68	27.0	1.65	26.0	1.62
4	21.4	1.91	20.8	1.88	12.0	2.24
5	33.0	1.48	30.6	1.53	34.0	1.44
6	28.4	1.68	27.0	1.69	26.6	1.68
7	26.3	1.78	26.1	1.75	23.6	1.84
8	24.5	1.86	23.6	1.84	14.1	2.36

Each numerical value is an average from 5 samples.

Table 15

Absorption and Bulk Density on Samples Fired to 1400° C. with a 12 Hour Soak

Composition No.	Oxides		Kaolin		Synthetic Minerals	
	Absorption (%)	Bulk Density (g/cc)	Absorption (%)	Bulk Density (g/cc)	Absorption (%)	Bulk Density (g/cc)
1	30.6	1.49	24.8	1.62	14.7	2.03
2	24.5	1.65	21.9	1.73	15.8	1.94
3	10.0	2.14	17.4	1.89	17.2	1.91
4	0	2.67	14.7	2.02	19.1	1.87
5	28.9	1.53	13.5	1.97	0	2.57
6	24.8	1.65	1.8	2.58	0	2.87
7	14.6	2.13	0.9	2.80	0	3.13
8	4.6	2.76	0.6	3.17	0	3.32

Each numerical value is an average from 5 samples.

Table 16

Modulus of Rupture on Samples Fired
to 1400° C. with a 12 Hour Soak

	Oxides	Kaolin
Composition No.	Modulus of Rupture (PSI)	Modulus of Rupture (PSI)
1	580	1,670
2	1,280	1,860
3	1,890	1,900
4	4,020	1,760
5	820	3,860
6	1,780	8,120
7	2,390	11,650
8	7,510	16,920

Each numerical value is an average
from 5 samples.

VIII. DISCUSSION

A qualitative examination of the X-ray patterns showed that equilibrium conditions have been approached minerallogically in all the specimens. This is especially true of the compositions in the anorthite-gehlenite-corundum composition triangle. No minerals other than these three could be distinguished in the X-ray patterns. In the anorthite-mullite-cristobalite sub-system, however, a small amount of corundum was still present in practically every case. Corundum according to the phase diagram is an incompatible phase in this triangle. When it is considered, however, that corundum reacts slowly at best and furthermore that a large amount of this material was added to each composition, it is not surprising that some corundum did not react. Plate 14, a typical example of compositions 1 through 4, shows clearly the gradual reduction in the amount of corundum in composition 3 as more and more heat treatment was given to the sample at 1400° C. When the sample first reached 1400° C. there was 38 percent corundum still left in the sample. A three hour soak at this temperature decreased the corundum content to 24 percent, and in six hours it was only 18 percent. Finally at twelve hours (table 10) only 3 percent of the original corundum remained. Therefore it can be assumed with considerable justification that if the specimens were

held at 1400° C. with longer and longer heat treatments, all the corundum would have eventually disappeared and only the compatible phases would be present in the sample.

Another point that might at first glance tend to discredit the statement that equilibrium conditions were approached in the anorthite-mullite-cristobalite compatibility triangle is that no cristobalite was found in the X-ray patterns. However, this can be explained by glancing at the $CaO-Al_2O_3-SiO_2$ ternary phase diagram. It will be noted that as compositions 1 through 4 are heated above the eutectic point at 1347° C., cristobalite and/or quartz disappears from the solid phase so that the solid phase consists entirely of mullite and anorthite. It is also known that the liquid formed in this part of the system is highly viscous.[16] Therefore, upon cooling, the crystallization of the liquid would be curtailed because its constituents would have little mobility and the liquid would remain as a glass. Eitel[17] brought this out when he said that the high viscosity of eutectic silicate melts leads easily to typical undercooling non-equilibria.

A similar phenomenon but with different results can be shown in the case of gehlenite in the compositions of the anorthite-gehlenite-corundum sub-system. Under ideal conditions gehlenite disappears from the solid phase when the compositions are heated above 1382° C. leaving only corundum

and anorthite. The liquid formed in this case, however, is
very fluid so that the chances of gehlenite recrystallizing
from the melt are very strong. That this actually happened
is illustrated by plate 13. Composition 8 prepared from
the oxides was taken as an example as it was typical of all
the compositions studied in this triangle. At 1400^{0} C.,
with no hold, the X-ray pattern of the quenched sample show-
ed gehlenite, indicating that little or no liquid had been
formed. After continued heating for 3/4 of an hour and
quenching in air, no gehlenite was distinguishable by the
X-ray. In all the samples that were quenched in air after
various holding times up to 12 hours there was no sign of
gehlenite in the X-ray patterns. It is evident that the
gehlenite was dissolved as the liquid formed. When the
samples were allowed to cool slowly with the furnace (Plate
11) gehlenite reappeared in the X-ray pattern. The petro-
graphic microscope gave further evidence of this occurence.
In the sample fired to 1400^{0} C. with no hold the gehlenite
crystals were too minute to be distinguished and there was
no evidence of any glass. Examination of the sample allow-
ed to cool slowly after a 12 hour hold at 1400^{0} C. revealed
large crystals of gehlenite which could easily be indentifi-
ed and also a small amount of glassy phase.

Quantitatively, the compositions in the anorthite-
gehlenite-corundum sub-system fired to 1400^{0} C. with a 12

hour hold and allowed to cool slowly with the furnace seemed from the evidence obtained to have attained equilibrium. This was especially true of the samples prepared from the oxides. The agreement between the quantitative X-ray measurements of compositions 5 to 8 (table 10) and the amounts predicted by the phase diagram (table 5) was very close. Samples of compositions 5 to 8 prepared from the oxides, that were quenched in air after they were held at 1400 $^{\circ}$ C for 12 hours gave further evidence that equilibrium was attained. Table 13 shows the close agreement between the amounts of the minerals when measured by the X-ray and the amounts of the minerals calculated from the equilibrium diagram at 1400 ^{b} C.

When experimental error and the limited amount of accuracy that can be obtained from quantitative X-ray measurements are taken into account there can be little doubt that equilibrium conditions had existed in the specimens of compositions 5 through 8 made from the oxides.

Unfortunately, no specimens of the compositions containing kaolin and those prepared from the synthetic minerals were quenched in air. Therefore the above statement cannot be made with as much certainty for these two groups. However, the theoretical amounts of the solid phases for each composition of these two groups were calculated from the

equilibrium diagram for the same percentage of glass or liquid phase as is shown in tables 11 and 12 and when the results were compared with the results of these tables they were found to be in excellent agreement.

Compositions 1 through 4 in the anorthite-mullite-cristobalite composition triangle did not approach equilibrium as closely as did compositions 5 to 8. As was stated previously this could be seen quantitatively by the presence of corundum in the X-ray patterns. Quantitatively, compositions 1, 2, and 3 made from the oxides, compositions 1, 2, 3, and 4 containing kaolin, and compositions 1, 2, 3, and 4 prepared from the synthetic minerals were in close agreement with the amounts called for in the phase diagram. Composition 4 made from the oxides was relatively much further away from equilibrium. It contained 58 percent mullite compared to 76 percent predicted from the phase diagram. The specimen was vitreous and translucent indicating that a good deal of liquid had been formed. This was confirmed by examining the specimen under the petrographic microscope. Large crystals of mullite indicating crystallization from a melt were indentified along with very tiny crystals of mullite and anorthite. A relatively large amount of glass was dispersed throughout the sample. Large crystals of mullite were also noticed

in compositions 1, 2, and 3 made from the oxides but here
there was a smaller amount of glass present. What apparent-
ly happened was the formation of increasingly greater amounts
of liquid as the compositions in the anorthite-mullite-
cristobalite sub-system approached more closely the comp-
ositions of mullite. It is generally know that in order
to synthesize mullite from corundum and quartz at temper-
atures below the fusion point, the mixture must be fired,
ground, and refired repeatedly before all the quartz and
corundum react. It is plausible to assume, therefore,
that equilibrium is more difficult to achieve in comp-
ositions that have large amounts of mullite such as
composition 4. Foster[11] in working with compositions in
the $MgO-Al_2O_3-SiO_2$ system also encountered difficulty in
synthesizing mullite which led him to say that the binary
mixture of alumina and silica seemed to be an exception
to the general case of high alumina compounds forming
readily at high temperatures. He added, however, that in
ternary compositions in which a small amount of magnesium
oxide was present, mullite formed readily and almost
quantitatively. This might be true of MgO but it does not
seem to apply as fully to CaO. It is true that mullite
forms more readily when CaO is present but it is far from
the amount predicted by the equilibrium diagram.

Composition 4 prepared from the synthetic minerals and also prepared using kaolin as the source of silica came much closer to equilibrium. This is not surprising because much of the mullite was supplied by the synthetic mullite and kaolin. The amounts of glass seen under the microscope were small and there were no large crystals of mullite as seen in the sample made from the oxides.

Foster[2] says there is ample justification for the premise that equilibrium can be very closely approached in the solid state. He also says that there is justification for assuming that, in some cases, ceramic reactions are entirely solid-state affairs. There can be little doubt that the compositions studied in the anorthite-gehlenite-corundum compatibility triangle attained equilibrium in this manner. Such was not the case with the compositions made from the oxides in the anorthite-mullite-cristobalite composition triangle. True, the anorthite was formed quantitatively in the solid state for each composition but the mullite did not seem to be formed in the solid state. X-ray patterns of compositions 1 to 4 fired to temperatures below 1400° C. showed no sign of mullite. It was only after having reached 1400° C. that there was any indication of mullite in any of the patterns. Liquid formation should start in this sub-system at 1347° C. but with the firing

rate used in this experiment it would probably start at a somewhat higher temperature. It appears that no mullite was formed until some liquid phase was produced in the samples. Plate 14 shows no mullite in composition 3 heated to 1400° C. with no hold. It did appear, however, in the X-ray pattern of a sample of this same composition held for 3/4 hours at 1400° C. (not shown). It is interesting to note when mullite was first seen in the X-ray patterns of compositions 1 through 4. In composition 1, where 16 percent mullite is called for by the equilibrium diagram, no mullite was seen until 14 percent of it appeared in the X-ray pattern of the sample held for 12 hours at 1400° C. In composition 4, 16 percent mullite appeared at 1400° C. with no hold, however, no mullite was seen at 1380° C. Equilibrium conditions require 76 percent mullite in composition 4.

Another interesting phenomenon is the persistance of silica in the form of quartz in compositions 3 and 4. It does not disappear until after 3 hours of heat treatment at 1400° C. In composition 1 and 2, however, quartz disappeared at 1360° C.

What this means it is not possible to say with the evidence at hand. Certainly more compositions should be studied in the anorthite-mullite-cristobalite triangle, especially at the high mullite end.

In general it can be said that equilibrium is approach-
ed more slowly by compositions in the anorthite-mullite-
cristobalite sub-system than by those in the anorthite-
gehlenite-corundum sub-system. It is probable that
equilibrium would be attained by the former if the specimens
were held at 1400° C. for a longer period of time.

The eutectic compositions in the wollastonite-anorthite-
gehlenite compatibility triangle when fired to 1250° C.
consisted chiefly of wollastonite and gehlenite with a very
small amount of anorthite (Plate 12). This composition
was mixed with corundum and quartz to form composition 7.
This sample was then fired to 1270° C. and quenched in air.
The X-ray pattern disclosed anorthite and corundum almost
in the amounts predicted by the phase diagram. There was
a slight excess of gehlenite but the wollastonite had
disappeared. When fired to 1400° C., held for 12 hours,
then quenched in air, the sample showed 39 percent anorthite,
51 percent corundum, and 10 percent glass. This is
practically indentical with the 37 percent anorthite, 53
percent corundum, and 10 percent liquid calculated from
the phase diagram.

From the X-ray patterns taken of the samples prepared
from the oxides at temperatures below 1400° C., it was
hoped that some idea of the crystallization path of the

Compositions would be attained. Kraner[18] has said that in any system the lowest eutectic or invariant point in the system will be the first to form as the temperature is raised. Foster[2] agrees with this but restricts it to those compositions made from the oxides. It must be remembered that the equilibrium diagram is based on reactions between minerals; therefore the above statements would be valid only if the mineral end members of the sub-system in which the lowest eutectic is located are present. This did not seem to be the case in the present study. For instance, calcium aluminate was present in all the compositions at $1200°$ C. and disappeared at $1300°$ C. The phase diagram reveals that the lowest eutectic concerning calcium aluminate in the $CaO-Al_2O-_3SiO_2$ system occurs at $1336°$ C. In compositions 1, 2, and 5 beta dicalcium silicate was also present a $1200°$ C. and disappeared at $1220°$ C. with the formation of wollastonite. At $1260°$ C. wollastonite disappeared and strong formations of gehlenite and anorthite became evident. Gehlenite seemed to form preferentially to anorthite in all the compositions at low temperatures disappearing in compositions 1 to 4 when $1400°$ C. was reached. In composition 3 and 4 no other non-equilibrium compounds were formed other than calcium aluminate and gehlenite. $CaO-2Al_2O_3$ replaced $CaO-Al_2O_3$ at $1300°$ C. in compositions

6, 7, and 8 which in turn was replaced at 1360° C. by a compound for which no information could be found in the A. S. T. M. X-ray card files. This compound disappeared at 1400° C.

Reference has been made in the literature to two calcium aluminates, namely $CaO \cdot 6Al_2O_3$[19] and $3CaO \cdot 16Al_2O_3$[20]. Mixtures made from the oxides in the theoretical porportions to form both of these compounds were fired to 1500° C. and held at this temperature for 24 hours. It was found that the X-ray lines corresponded to the unknown lines found in compositions 6, 7, and 8. The X-ray pattern of the $CaO \cdot 6Al_2O_3$ mixture showed the presence of free corundum while in the X-ray pattern of the $3\ CaO \cdot 16Al_2O_3$ mixture no other phases other than the unknown compound were seen. Therefore the formula of this compound in all probability corresponds more closely to $3CaO \cdot 16Al_2O_3$. The evidence seems to indicate that such a compound does exist in the $CaO \cdot Al_2O_3 \cdot SiO_2$ system but it is outside the scope of this investigation to make any predications as to its stability relations in the system.

The compounds formed at low temperatures progressed from binary compounds containing a high percentage of calcium oxide to those containing less - $2CaO \cdot SiO_2$ to $CaO \cdot SiO_2$ and $CaO \cdot Al_2O_3$ to $CaO \cdot 2Al_2O_3$ to $3\ CaO \cdot 16Al_2O_3$-

until finally the ternary compounds were formed. In all
cases the amount of these compounds in the sample, other
than the equilibrium phases, was small.

H. S. Yoder[10] found the same order prevailing in the
formation of the silicate compounds from a mixture of
calcite, quartz, and beta alumina in the wollastonite-
anorthite-gehlenite composition triangle. In his experiment
the compounds were formed at much lower temperatures
(600°C to 1000°C) but he held the mixture at each temper-
ature for 500 hours. He found only the equilibrium phases at
900° C. and 1000° C.

Absorption and bulk density are of little value in
determing the approach to equilibrium. These values serve
however to illustrate the marked difference in physical
properties of samples having the same ultimate composition
but compounded of different raw materials.

IX. CONCLUSIONS

Based on the results of the present investigation the following conclusions seem justified:

(1) Equilibrium is attained by compositions in the anorthite-gehlenite-corundum compatibility triangle when held for twelve hours at 1400° C.

(2) Equilibrium is closely approached but is not attained by compositions in the anorthite-mullite-cristobalite compatibility triangle when held for twelve hours at 1400° C.

(3) The reactions in the anorthite-gehlenite-corundum sub-system take place essentially in the solid state.

(4) The transitory compounds that are formed at temperatures below 1400° C. progress from the binary compounds of dicalcium silicate and calcium aluminate to binary compounds of higher silica and alumina contents, respectively, until gehlenite and anorthite are formed.

(5) The introduction of incompatible phases such as wollastonite and mullite does not deter the attainment of equilibrium in the anorthite-gehlenite-corundum triangle.

(6)   Absorption and bulk density are not good indicators of the attainment of equilibrium in the compositions studied, but serve to show the marked differences in physical properties of samples having the same ultimate composition but made from different raw materials.

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XI. BIBLIOGRAPHY

1. J. W. Mellor, "Some Chemical and Physical Changes in the Firing of Pottery," J. Soc. Chem. Ind., 26(8)375-377 (1907).

2. W. R. Foster, "Contributions to the Interpretations of Phase Diagrams by Ceramists," J. Am. Ceram. Soc., 34(5)151-160 (1951).

3. F. P. Hall and H. Insley, "Phase Diagrams for Ceramists," J. Am. Ceram. Soc., 30 (Part II, 152 pp.) (1947).

4. Composition-Temperature Phase Diagrams of the Refractory Oxides (Four Plates). Revised and redrawn by R. B. Sosman and Olaf Anderson. Research Laboratory, U. S. Steel Corp., Lincoln Highway, Kearny, N. J.

5. F. H. Riddle, "Ceramic Spark-Plug Insulators," J. Am. Ceram. Soc. 32(11)333-346 (1949).

6. W. R. Foster and H. F. Royal, "Intermediate Compound in the System $BeO \cdot Al_2O_3$(crysoberyl)-Al_2O_3(corundum)," J. Am. Ceram. Soc. 32(1)26-34 (1949).

7. R. A. Morgan and F. A. Hummel, "Reactions of BeO and SiO_2; Synthesis and Decomposition of Phenacite," J. Am. Ceram Soc., 32(8)250-255(1949).

8. N. L. Bowen, "Petrology and Silicate Technology," J. Am. Ceram. Soc., 26(9)285-301 (1943).

9. J. R. Goldsmith and E. G. Ehlers, "Stability Relations of Anorthite and its Hexagonal Polymorph in the System $CaAl_2Si_2O_8$-H_2O," J. of Geol., 60(4)386-397 (1952).

10. H. S. Yoder, "Stability Relations of Grossulerite," J. of Geol., 58(3)221-253 (1950).

11. W. R. Foster, "Synthetic Sapphirine and its Stability Relations in the System MgO-Al_2O_3-SiO_2, J. Am. Ceram. Soc., 33(3)73-84 (1950).

12. G. A. Rankin and F. E. Wright, "Ternary System CaO-Al_2O_3-SiO_2," Amer. J. Sci., 39,1-79 (1915); N. L. Bowen, "Petrology and Silicate Technology," J. Am. Ceram. Soc., 26(9)285-230 (1943).

13. M. A. Tuttle and R. L. Cook, "Fundamental Study of Crystalline and Glassy Phases in Whiteware Bodies," J. Am. Ceram. Soc., 32(9)279-294 (1949).

14. P. Duwez and F. Odell, "Quantitative Analysis of Cubic and Monoclinic Zirconia by X-ray Diffraction," J. Am. Ceram. Soc., 32(5)180-182 (1949).

15. S. C. Sane and R. L. Cook, "Effect of Grinding and Firing Treatment on Whitewares," J. Am. Ceram. Soc., 34(5)145-151 (1951).

16. J. S. Machen and Ten Boo Yee, "Viscosity Studies of System $CaO-MgO-Al_2O_3-SiO_2$: II, $CaO-Al_2O_3-SiO_2$," J. Am. Ceram. Soc., 31(7)200-204 (1948).

17. W. Eitel, "Silicate Melt Equilibria," Par. 89, Rutgers U. Press, (1951).

18. H. M. Kraner and S. J. McDowell, "Talc as the Principal Body Ingredient in Vitrified Ceramic Bodies," J. Am. Ceram. Soc., 8(10)626-635 (1925).

19. N. E. Filonenko and I. V. Lavrov, "Calcium Hexaluminate in the System $CaO-Al_2O_3-SiO_2$," Doklady Akad. Nank SSSR66(4)673-676 (1949), Ceram. Abstracts, 29, p. 2J (1950).

20. K. Lagerquist, S. Wallmark, and A. Westgren, "X-ray Investigation of the $CaO-Al_2O_3$ and $SrO-Al_2O_3$ System," Z. Anorg. u. allgem. Chem., 234, 1-16 (1937); Refractories Bibliography, p. 1031 i, published by the American Iron and Steel Institute (1950).