CHARACTERISTICS OF A VIRGINIA KYANITE

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I. INTRODUCTION

For many years the mineral kyanite has been mined in various parts of the world. The ore deposits have not been worked with any great enthusiasm since the commercial possibilities of kyanite have only been theorized as a result of laboratory experiments. Several large deposits of kyanite have been located in recent years; and this supply, which is sufficient to meet the demands of the ceramic industries, has created an interest in the possibilities for kyanite. The physical properties of kyanite make it both desirable and objectionable for use in certain fields of ceramics. The objectionable properties, however, have been overcome to some extent, making it possible for this mineral to find wide application in the field of refractories.

The largest deposit of kyanite found in Virginia is located in Prince Edward County. The ore deposit is known as the Baker Mountain deposit and is sufficiently large to supply any demands of the ceramic industries. The ore mined there is processed by froth flotation and magnetic separation. This process has consistently yielded a kyanite concentrate containing 93 per cent pure kyanite. Acid-washing of the kyanite concentrate has produced even purer grades for commercial use.

This investigation was undertaken to study the physical characteristics of this Virginia kyanite both before and after heat treatment.

II. REVIEW OF LITERATURE

Mineralogy

Kyanite is a member of the sillimanite group of which andalusite and sillimanite are also members. It has the same chemical composition as andalusite and sillimanite, having the formula $Al_2O_3.SiO_2$. It differs from andalusite and sillimanite only in that it crystallizes in the triclinic system instead of the orthorhombic system, and has a higher specific gravity of 3.5 to 3.7 as compared with 3.1 to 3.2 for andalusite and with 3.2 to 3.3 for sillimanite.

The kyanite of the Baker Mountain deposit occurs in a quartzite schist. This deposit contains the massive-type kyanite quartzite, which occurs abundantly, and also small, needle-like masses of radiating crystals in quartzite. There are included in this schist small amounts of muscovite, rutile, hematite, pyrite and quartz. Most of these minerals are eliminated by the concentration process and by magnetic separation. This Virginia kyanite occurs as deep greenish-blue, blade-like crystals, while andalusite varies from white through gray to pinkish brown. The Virginia kyanite has a hardness of 4 to 5 parallel to the blade and 6 to 7 across the blade, whereas, andalusite has a hardness of 7 to 7.5. The tenacity of these minerals varies: kyanite being brittle and andalusite varying from brittle to hard.

An extensive study of all available literature was made by the author and it was found that many investigators have used kyanite in the various fields of ceramics. The kyanite used in these investigations was, in many cases, not the pure grades of kyanite now available and the work was not always carried to a final conclusion. Listed below under suitable headings are the results of the work of investigators interested in a particular ceramic field.

Glass

Scholes[1], in an investigation on the uses of kyanite as a source of alumina in commercial glasses, found that kyanite, if properly prepared, meets the requirements for commercial glasses excellently and offers specific advantages over the alumina supplying materials now in use. In discussing the favorable characteristics of kyanite as a constituent in glass batches he lists the following points:

1. Kyanite is prepared from the original rock or mineral deposit in a pulverulent or granular condition. The particles are non-adherent, and the material will not segregate in balls or lumps as kaolin does, nor exhibit the fluffy, floating character of alumina hydrate. It behaves physically like glass sand.
2. In its process of preparation, kyanite can be reduced to an iron oxide content well below 0.1 per cent, with not more than traces of other heavy minerals. Since its alumina content is easily three times that of feldspar, only one-third as much need be added in the batch, and the quantity of iron oxide will be as low as with a feldspar containing 0.33 per cent Fe_2O_3.
3. Modern methods of refining produce a kyanite of alumina content constant within 1.5 per cent, equivalent to a felds-

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1. Scholes, S. R., "Kyanite as a Cheap Source of Alumina for Commercial Glasses", Ceramic Age, February, pp. 54 (1938).

par with a constancy of 0.5 per cent. The impurities present in kyanite are almost entirely silica, which offers no difficulties. Bases are absent.

4. Kyanite is prepared by a relatively cheap process which, in view of its high alumina content, offers substantial economies in comparison with other aluminous materials of equal purity.
5. The available supply is very large.
6. It has been found that kyanite dissolves readily in a glass melt in which it is a batch ingredient, provided it is ground to a fineness of about 60-mesh.

It was found that finely ground, refined kyanite will readily dissolve in a glass melt without any traces of undissolved mullite, if commercial glass, with an alumina content as high as current practice requires, is made with kyanite as the aluminous ingredient of the batch. This is a decided economic advantage and furnishes a new effective means of introducing alumina into commercial glasses, thereby, securing in a cheap and efficient manner, the beneficial effects of alumina upon the strength, viscosity, chemical durability and thermal endurance of the glasses.

For proper use, the kyanite should be ground preferably to 60-mesh, but in large scale melting a coarser granulation might be used, such as, 20-mesh. However, the grinding should be fine enough so that thorough dissemination of the aluminous material takes place throughout the batch and renders the resulting glass homogeneous. As the inversion of kyanite to mullite and silica involves an expansion of about 10 per cent in volume, these crystals offer a relatively large surface for attack, and dissolve readily in the melting batch. This allows for coarser granulation in large-scale melting.

In a further investigation, presented anonymously[2], on the use of kyanite as a glass material, it has been found that the alumina content of kyanite requires that less of this material be used than is the case with some other sources of alumina. Also, the balance of the composition, silica, is a natural raw material of glass and the absence of alkalies virtually causes only a minimum of adjustment in the batch. Kyanite is added to the batch at approximately 100°F. higher temperature, thus increasing the speed of the operation. As a result of using kyanite as a source of alumina, new wares and shapes have been reported as being possible to manufacture. The work of this investigation is analogous to that of Scholes.

An article by Weis[3] explained why it is not possible to use kyanite as an ingredient in glass batches. He states that because of the varying percentages of alumina, the amount of impurities, such as iron, are higher than in feldspar, and kyanite is too refractory a material for use in glass batches. He does, however, recommend the use of kyanite in glass tank blocks.

Refractories

In the use of kyanite in refractories Greig[4] found an advantageous factor in that kyanite inverts to mullite on heating, and once the inversion has taken place it is not reversible. Freed[5] found that mullite,

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[2] Scholes, S. R., ''Kyanite - A New Glass Material'', Ceramic Industry, Vol. 20, No. 4, pp. 177, (1933).

[3] Weis, J. H., ''Comments on Kyanite as a Glass Material'', Ceramic Industry, Vol. 20, pp. 235 (1933).

[4] Greig, ''Formation of Mullite from Kyanite, Andalusite and Sillimanite, Jour. Am. Cer. Soc., Vol. 8, pp. 465 (1925).

[5] Freed, ''A Study of Mullite Refractories Formed by Calcining Kyanite, Their Industrial Application'', Jour. Am. Cer. Soc., Vol. 9, pp. 251 (1926).

pure or bonded with clay, formed by calcining kyanite produced refractory bodies capable of withstanding standard and modified laboratory tests for high grade refractories. The bodies produced by him were highly refractory and showed excellent resistance to deformation under load and spalling. He also found a uniform rate of thermal expansion. The results of this investigation indicate that the prospects for development of mullite as a so-called ''super-refractory'' appear bright.

In an investigation on the use of sillimanite minerals in refractories, published anonymously[6], the results indicate that electric porcelains and saggers containing kyanite have a much longer life than those made from ordinary mixtures. Further work, presented anonymously[7] has indicated that with similar treatment the products made from the three sillimanite minerals are identical irrespective of which mineral is used. Many experiments have been made using calcined material alone, or mixed with ball clay, or ball clay and feldspar, or calcined alumina. Mixtures of calcined and raw kyanite were used with 5 per cent ball clay added. The addition of feldspar gave a vitrified product, though the refractoriness was above Cone 28 (1615°C. approx.), even with ten parts feldspar in 115. A mixture of 76.1 per cent calcined kyanite with 23.9 per cent alumina (calcined at 1650°C.) gave brick which showed practically no shrinkage and was of good texture. Refractories made from calcined kyanite have been reported, anonymously[8], to have a high mechanical resistance and will withstand the reducing or oxidizing action of gas, carbon and slag.

As an ingredient in crucibles for glass melting, Scholes[9], found

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[6] Anonymous, "Andalusite Minerals in Refractories", Ceramic Abstracts, Vol. 9, pp. 848 (1930).

[7] Anonymous, "Sillimanite", Ceramic Abstracts, Vol. 9, pp. 942, (1930).

[8] Anonymous, "Sillimanite and Its Use as a Super-Refractory", Ceramic Abstract, Vol. 16, A(6) 177 (1937).

[9] Scholes, S. R., "The Use of Kyanite in Crucibles for Glassmelting", Bull. Am. Cer. Soc., Vol. 14, No. 10, pp. 335-36 (1935).

that 60-mesh calcined kyanite, which consists essentially of mullite and some crystalline form of silica, presumably tridymite, mixed with a refractory ball clay, known as "XX sagger", in the proportions of 65 per cent kyanite and 35 per cent clay, and formed into a slip with the addition of 0.2 per cent by weight of alkali, which is equal parts of sodium carbonate and sodium silicate θ "S" brand, produced a crucible which met adequately the requirements of the operation. The slip casted into gypsum molds developed a wall thickness of approximately 3/8 inch in 5 to 10 minutes. The sizes commonly made range from $2\frac{1}{2}$ inches to 7 inches in heighth; however, as the dry strength of the resulting body is not very great the dry crucibles must be handled carefully.

Upon firing to Cone 4 (1210°C. approx.), the crucibles develop excellent mechanical strength with a total of 5 to 8 per cent shrinkage from mold size to the fired condition. The resulting crucibles may be heated to redness in 20 minutes and thereafter brought up to the glass melting temperature as rapidly as necessary without danger of breakage. The crucibles are nearly white and the low iron content, together with limited corrosion, enables most glasses to be melted without appreciable iron contamination.

The crucibles were able to withstand rapid heating; therefore, they have good thermal endurance, low expansion and high strength. They were sufficiently non-porous to prevent penetration by the molten glass and consequently rapid corrosion.

In the use of kyanite as a lining for pot and tank furnaces, Litvakovskii[10] found that kyanite linings resist well the attack of the glass

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[10] Litvakovskii, "Application of Highly Refractory Sillimanite Materials In the Glass Industry", Ceramic Abstract, Vol. 15, pp. 63 (1936).

mass, and that the character of the corrosion is different from that appearing in grog brick. Grog mixes obtain a "shell-like" appearance on their surface, while kyanite linings become only uniformly thinner. In an attempt to produce a kyanite lining for the protection of refractories for glass tanks, Ruibnikov[11] reported that a lining of composition 65 to 85 per cent kyanite, 14.5 to 30 per cent clay, 5 to 10 per cent feldspar and 2.5 to 5.0 per cent sodium silicate had the following properties:

1. A kyanite refractory lining with a low water absorption (5.9 to 9.0 per cent), high mechanical strength (849 to 506 kg/sq cm), a refractoriness of 1735 to 1710°C. and an alumina content from 41.4 to 44.3 per cent and can be successfully used for coating grog brick.
2. The alumina content can be increased provided that the clay flux content is lowered and the temperature of firing is above 1400°C.

Blocks of ordinary composition containing 85 per cent grog and 15 per cent clay were coated by ramming, dried and fired to 1380 or 1410°C. Experiments showed that the adherence of kyanite coats to grog brick was satisfactory.

In a study of the mullite content of some American tank blocks by Thompson and Vormelker[12], the conclusion was drawn that the presence of mullite in a tank block will lengthen its life by increasing the resis-

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11. Ruibnikov, "Kyanite Coating for Tank Blocks With a High Grog Content," Ceramic Abstract, Vol. 15, pp. 243 (1936).
12. Thompson and Vormelker, "The Mullite Content of Some American Tank Blocks", Jour. Am. Cer. Soc., Vol. 9, pp. 639 (1926).

tance of the glass block to corrosion or chemical action of the molten glass and the glass batch. The alumina and silica present in a tank block tend to form the mineral mullite when the block is fired to a sufficiently high temperature. This conclusion follows from the thorough study of the problem by Bowen and Greig[13].

Rees[14] in his paper of "Alumina-Silica Minerals in Glass House Pots and Tanks" gave the following conclusions:

1. That the alumina-silica mineral found in fire clays after firing has the composition $3Al_2O_3 \cdot 2SiO_2$ and is called mullite. This agrees with the work of Bowen and Greig.
2. The proportion of mullite present in fired clay increases with the alumina content of the clay and with the temperature and duration of the heat treatment.

Porcelain

McDowell and Vachuska[15] in studying the effect of calcined Virginia kyanite in porcelain bodies concluded that mullite introduced from a calcined kyanite ground to a proper fineness and introduced in feldspar, flint, clay porcelain bodies in amounts over 30 per cent had the following effects on the physical properties of the bodies:

1. Increase in modulus of rupture
2. Decrease in coefficient of expansion
3. Increase in firing time required
4. Increase in firing range
5. Color graduation of from white to gray due to iron bearing accessory minerals.

It is required that 30 per cent or more of the material be used to produce marked changes of the bodies due to the fact that there is little

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[13] Bowen and Greig, "The System: $Al_2O_3.SiO_2$", Jour. Am. Cer. Soc., Vol. 7, pp. 238 (1924).

[14] Rees, W. J., "Alumina-Silica Minerals in Glass House Pots and Tank Blocks", Jour. Soc. Glass Technology, December, 1925.

[15] McDowell, S. J. and Vachuska, "The Effect of Calcined Kyanite in Porcelain Bodies", Jour. Am. Cer. Soc., Vol. 10, pp. 64 (1927).

or no seeding effect, i.e., secondary mullite growth, from kyanite grains. These apparently act merely as inert particles with desirable physical properties.

In an investigation on special spark-plug porcelains, Bleininger and Riddle[16] found that it was desirable to eliminate the quartz because of its inversions and to substitute substances not subjected to inversions or other volume changes. These may be highly calcined kaolin, alumina, zirconia, or sillimanite, either natural or synthetic.

The results of an investigation on the use of kyanite in porcelain bodies, published by Kulki[17] indicate that additions of 35 per cent to 50 per cent of calcined kyanite have the following effects on the porcelain mixes: increases (1) their mechanical strength, (2) dielectric properties at normal and high temperatures, (3) resistivity to sudden temperature changes, and (6) thermal resistivity.

Saggers

Because of the high losses encountered in the production and handling of saggers, there have been many additions to sagger mixes investigated. Makhl[18] found that admixtures of kyanite and andalusite have no marked effect on the properties of saggers; however, the fact that low grade kyanite and andalusite were used must be considered. The results of this work do not agree with those of Loomis[19] who found that bodies containing finely ground calcine kyanite, talc, Georgia kaolin, and Ohio

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16. Bleininger, A. V. and Riddle, F. H., "Special Spark Plug Porcelains", Jour. Am. Cer. Soc., Vol. 2, pp. 564 (1919).
17. Lulki, A., "Using Kyanite in the Russian Ceramic Industry", Ceramic Abstracts, Vol. 12, pp. 383 (1933).
18. Makhl, R., "Effect of Highly Refractory Additions to Sagger Mixes", Ceramic Abstracts, Vol. 17, No. 7, pp. 253 (1938).
19. Loomis, G. A., "Notes on Sagger Investigation", Ceramic Age, July, pp. 9 (1934).

fire clay had the highest fired strength of the series, little or no tendency to sag at high temperatures, and good heat-shock resistance, but were not the best of the series in the last mentioned property.

In a laboratory investigation, conducted anonymously[20], to determine the value of kyanite sagger mixes it was found that, in general, the drying, firing, and total shrinkage decrease with an increase in the amount of kyanite. The exception is found in the series where kyanite is substituted for grog. In this case all the above mentioned factors increase as the amount of kyanite increases.

The raw modulus of rupture shows no surprising results in that little variation is produced within any one series. The results indicate the value of the bond clay in that as it varies the modulus varies directly. The exception to this is again found in the series where the grog is varied. Here an increased modulus is noted, probably due to the higher percentage of fine particles where the kyanite replaces the grog. The water absorption consistently decreases as the amount of kyanite increases, though not by overwhelming percentages. The water of plasticity does also decrease somewhat as the amount of kyanite increases.

It is to be noted that drying and firing cracks are not noticeable on the kyanite bodies; whereas they are very much in evidence on the original sagger mix. The strength of the bodies at this point was not tested because of inadequate means.

Grog

In attempting to produce a kyanite grog, presented anonymously[21], it was found that by using kyanite fines with 4 per cent talc and 2 per cent

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[20] Anonymous, Personal Correspondence Between H. S. Doty and United Clay Mine Company.
[21] Anonymous, "Kyanite", Ceramic Age, January, pp. 24 (1938).

bentonite the resulting batch had good working properties with no apparent loss in refractoriness. This material gave an excellent grog that would withstand well the 25 cycles of heating and chilling demanded in glass-tank block specifications. In fact, 35 cycles between 850°C. and room temperature were used as a test. As the bats fired for grog production were in the form of bricks, their expansions were measured. It was found that the mix of kyanite flotation concentrate with 4 per cent talc and 2 per cent bentonite fired at 1650 to 1700°C. would retain the same dimensions as the original pressed shape.

This made possible a kyanite brick of very high kyanite content and excellent heat-shock characteristics, with an ultimate porosity below 20 per cent if a pressure of 10,000 lbs. per sq. in. (on a 4 inch column) was used. Only with kyanite fines of the size of flotation concentrate is this possible.

Insulating Brick

A high insulating material has been produced by Bole[22] by molding a mass constituted of sized raw kyanite and a small amount of clay to which hasbeen added sufficient chemical and dilute acid solution to produce bloating of the mass. By drying the molded mass and firing it at a sufficiently high temperature and at a rate to produce a highly cellular mass, a high insulating material can be produced.

The results of a recent investigation conducted by Pole and Moore[23] indicate that the production of insulating refractories can be made successfully from kyanite, clay and sawdust compositions. These compare favorably in many respects with commercial types of insulating brick.

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22. Bole, G. A., "High Insulating Material", Ceramic Abstract, Vol. 16, No. 5, P(5) 153, (1937).
23. Pole, G. R. and Moore, D. G., "The Expansion Characteristics of Kyanite and Kyanite-Clay Mixtures When Heated", Bull. Am. Cer. Soc., Vol. 17, No. 9, pp. 355-67 (1938).

III. EXPERIMENTAL PROCEDURE

Selection of Bonding Agents

In selecting the bonding agents to be used in forming the small test cylinders, consideration was given to the properties possessed by suitable materials. As kyanite is a non-plastic material, the bonding agents selected must possess a high degree of plasticity to develop a high bonding strength both in the dry and fired state. Their economic value was also considered in choosing the bonding agents used.

The bonding agents chosen and the percentages used were as follows:

Bentonite - 1%, 1.5%, 2%, 2.5%, 3%
Dextrine - 1.5%, 2%, 2.5%, 3%, 3.5%
Sodium Silicate - .5%, 1%, 1.5%, 2%, 2.5%, 3%
*Ballclay - 1%, 2%, 2.5%, 3%, 3.5%, 4%
Incorporated together
  Bentonite - 2%
  Talc - 4%

*No. 5 Tennessee Ball Clay - 200 mesh

Preparation of the Bodies

The percentage of kyanite used in the bodies was very high, ranging from 99.5 per cent to 96 per cent. As kyanite is a non-plastic material, thorough mixing of the batches was necessary to insure a homogeneous distribution of the bonding agents throughout the batch. To assure that this would be accomplished, batches of considerable size were used. A laboratory dry pan was used for dry mixing the batches, and the necessary percentage of water was added slowly to the thoroughly mixed batch while in the mixer. Upon thorough mixing and addition of the water, the wetted batches were passed through a 16-mesh sieve to reduce the lumps to a uniform particle size.

Forming and Firing

The test specimens were formed under 3000 pounds per square inch pressure in a small hydraulic dry press. A pressure of 3000 pounds per square inch was found to be sufficient to give a compact specimen which could be handled easily in the dry state. In forming the small cylinders, it was found that 10 per cent water gave the best results, with the exception of 3.5 per cent and 4 per cent ballclay. For these two percentages it appeared that 12 per cent water gave the best results.

Previous to firing, the samples were air dried and then at 110°C. for five hours. A specimen from each percentage of bonding agent used was fired to 2200°F., 2300°F., 2400°F., 2500°F., and 2600°F. as the reaction of raw kyanite at these temperatures was desired. The final temperature in each case was held for a period of one hour. A soaking period of one hour at the end of each firing was allowed for the formation of any glass and mullite growth to become evident or complete. The rate of firing was 150°F. per hour.

Tests Performed on Fired Samples

The fired specimens were tested for expansion, apparent specific gravity, bulk specific gravity, absorption, and apparent porosity at each of the temperatures ranging from 2200°F. through 2600°F. These tests were performed according to the procedure as given in the Journal of the American Ceramic Society. Test cones made from raw kyanite were subjected to the P.C.E. test outlined in the Journal of the American Ceramic Society, 11, 449, (1928)(previously mentioned publication).

Determination of Tightest Packing Between 35-Mesh and 100-Mesh Kyanite

A series of tests were performed using 1200 gram samples to determine the degree of packing of the 35-mesh and the 100-mesh kyanite. This was done by varying a combination of the percentages of these two mesh sizes from 0 to 100 per cent, and vibrating them at a constant rate until the packing had become constant. Two series of tests were performed: first, 35-mesh and 100-mesh raw kyanite; second, 35-mesh and 100-mesh calcined kyanite.

The purpose of performing such tests was to determine the combination of the percentages of these two mesh sizes that would give the tightest packing. The data obtained gave the mixtures that had a minimum of pore space between the grains prior to the addition of a bonding agent. This made possible the use of small percentages of bonding agents. Also, by having a minimum of pore space, a minimum pressure of 3000 pounds per square inch pressure was possible in forming the specimens.

Petrographic Examination

A petrographic examination was made on Baker Mountain kyanite concentrate to determine the state of the contained iron and the presence of any undesirable minerals. An analysis was made on all samples received from the mine; namely, raw and calcined standard and acid-washed grades of kyanite.

A study of powdered samples fired through the temperature range of 2200^{o}F. through 2600^{o}F. was made. The powder was obtained by crushing a sample fired to each temperature passing the powder through a 100-mesh sieve and using that material which was retained on a 200-mesh sieve.

Spectrographic Examination

A grating spectrograph of the Rowland Mounting type was used in making a spectrographic analysis of the Virginia kyanite. The radius of curvature of the concave grating was 181 cm. and the grating was ruled to have 14,438 lines/in. The theoretical dispersion of this grating was 9.7 Angstroms/cm. while the actual dispersion was 9.4 Angstroms/cm. The resolving power of this grating was 30,000 in the first order. The Rowland mounting uses a fixed slit which was opened 0.05 cm.

IV. PRESENTATION OF DATA AND CURVES

The data obtained in this investigation are found in Tables I-VII. A graphical representation of the data is found in Figures 1-9.

Table I lists the fired properties of the bodies at 2200°F.

Table II lists the fired properties of the bodies at 2300°F.

Table III lists the fired properties of the bodies at 2400°F.

Table IV lists the fired properties of the bodies at 2500°F.

Table V lists the packing properties of 35-mesh and 100-mesh raw raw kyanite.

Table VI lists the packing properties of 35-mesh and 100-mesh calcined kyanite.

Table VII lists the chemical analyses of standard and acid-washed kyahite.

The values used in the graphical representation of the data are those values in which the maximum percentage of bonding agent was introduced.

Fig. 1 shows the per cent expansion of the samples containing a maximum of bonding agent.

Fig. 2 shows the apparent specific gravity through the temperature range.

Fig. 3 shows the dry bulk specific gravity.

Fig. 4 shows the fired bulk specific gravity.

Fig. 5 shows the apparent porosity of the fired samples.

Fig. 6 shows the absorption of the fired samples.

Fig. 7 shows the data of Table V in graphical form.

Fig. 8 shows the data of Table VI in graphical form.

Fig. 9 shows the firing curve used in this investigation.

TABLE I

FIRED DATA
(2200°F)

*Specimen No.	Expansion %	App. Porosity %	Absorption %	App. Sp. Gr.	Bulk Sp. Gr. Dry	Bulk Sp. Gr. Fired
*111	-3.99	32.71	14.49	3.36	2.18	2.26
121	-3.32	32.35	14.29	3.35	2.21	2.26
131	-0.48	29.07	12.77	3.21	2.30	2.28
141	0.00	29.59	13.10	3.21	2.27	2.26
151	0.00	29.26	12.74	3.25	2.31	2.29
211	-1.42	33.02	14.95	3.30	2.22	2.21
221	0.72	31.17	12.01	3.19	2.26	2.20
231	-0.46	33.02	14.93	3.30	2.26	2.21
241	0.00	32.87	14.87	3.29	2.28	2.21
251	-0.52	33.82	14.95	3.34	2.28	2.36
261	-1.02	33.13	14.96	3.31	2.27	2.21
311	0.49	30.14	13.45	3.21	2.27	2.24
411	0.51	32.31	14.64	3.26	2.23	2.21
421	-0.50	31.28	14.06	3.24	2.23	2.23
431	0.00	29.46	12.89	3.24	2.30	2.29
441	-1.83	33.40	14.26	3.52	2.32	2.34
451	0.00	28.48	12.32	3.27	2.32	2.31
461	0.44	28.26	12.21	3.23	2.34	2.31
511	-0.24	35.32	16.50	3.31	2.15	2.14
521	-0.75	34.19	15.74	3.30	2.17	2.17
531	-0.45	34.68	16.05	3.31	2.16	2.16
541	-0.45	34.25	15.82	3.29	2.16	2.17
551	-0.45	32.66	14.87	3.26	2.19	2.20
561	-0.92	32.22	14.61	3.25	2.19	2.20

*The specimen numbers have the following significance:

First digit - Series
Second digit - Percentage (Shown under Procedure)
Third digit - Specimen number

Series 1 - Bentonite
Series 2 - Dextrine
Series 3 - Bentonite and Talc
Series 4 - Ballclay
Series 5 - Sodium Silicate

For example: Specimen 211 indicates a Dextrine bond, in amount of 1%;
Specimen 561 indicates a Sodium Silicate bond, in amount of 6%

TABLE II

FIRED DATA
(2300°F)

Specimen No.	Expansion %	App. Porosity %	Absorption %	App. Sp. Gr.	Bulk Sp. Gr. Dry	Bulk Sp. Gr. Fired
112	0.00	24.96	15.15	3.24	2.18	2.23
122	1.13	31.70	14.68	3.16	2.19	2.16
132	1.63	29.34	13.09	3.17	2.29	2.24
142	1.85	29.55	13.24	3.17	2.27	2.10
152	1.85	29.59	13.19	3.19	2.30	2.11
212	0.24	32.51	14.97	3.23	2.22	2.18
222	1.44	32.06	14.95	3.24	2.26	2.18
232	0.47	34.38	15.79	3.32	2.24	2.18
242	1.67	33.18	15.38	3.23	2.26	2.16
252	1.72	33.22	15.34	3.24	2.28	2.17
262	0.94	33.16	15.33	3.26	2.29	2.18
312	1.71	30.45	11.33	3.11	2.21	2.16
412	1.49	31.51	14.51	3.17	2.23	2.17
422	1.24	30.61	13.82	3.19	2.25	2.21
432	1.18	29.15	12.98	3.17	2.29	2.25
442	1.40	28.29	12.55	3.17	2.32	2.28
452	0.89	29.36	12.31	3.18	2.31	2.18
462	1.11	28.26	12.31	3.20	2.31	2.30
512	0.70	33.50	15.61	3.23	2.17	2.15
522	1.22	35.04	16.46	3.28	2.17	2.13
532	0.95	34.26	16.06	3.25	2.16	2.13
542	0.45	34.62	16.08	3.29	2.17	2.15
552	0.00	32.73	15.03	3.24	2.19	2.18
562	0.46	32.61	14.57	3.17	2.19	2.17

TABLE III

FIRED DATA
(2400°F)

Specimen No.	Expansion %	App. Porosity %	Absorption %	App. SP. Gr.	Bulk Sp. Gr. Dry	Bulk Sp. Gr. Fired
113	5.91	31.67	15.41	3.01	2.19	2.06
123	5.52	31.40	15.23	3.00	2.19	2.06
133	7.28	29.28	13.84	2.99	2.28	2.12
143	7.69	29.65	14.15	2.98	2.27	2.10
153	8.31	30.02	14.23	3.02	2.30	2.11
213	7.88	33.68	16.56	3.07	2.24	2.03
223	8.63	33.64	16.55	3.06	2.26	2.08
233	8.09	34.32	16.98	3.08	2.25	2.02
243	7.94	34.20	16.81	3.09	2.27	2.03
253	8.01	33.62	16.53	3.09	2.28	2.03
263	7.34	34.17	16.79	3.09	2.28	2.04
313	9.43	23.32	11.33	2.68	2.22	2.06
413	6.63	33.36	16.26	3.08	2.22	2.05
423	7.25	31.35	14.96	3.05	2.27	2.10
433	7.58	29.25	13.92	2.97	2.28	2.10
443	6.83	28.44	13.27	2.70	2.31	2.14
453	5.67	28.07	12.88	3.03	2.32	2.18
463	5.58	28.12	12.79	3.06	2.34	2.20
513	6.16	34.06	16.82	3.07	2.16	2.03
523	8.06	35.39	17.73	3.09	2.17	2.00
533	7.10	34.60	17.20	3.08	2.16	2.01
543	5.24	33.43	16.49	3.05	2.15	2.03
553	6.33	32.94	16.18	3.04	2.17	2.04
563	5.63	31.02	15.01	3.00	2.19	2.07

TABLE IV

FIRED DATA
(2500°F)

Specimen No.	Expansion %	App. Porosity %	Absorption %	App. Sp. Gr.	Bulk Sp. Gr. Dry	Fired
114	55.76	40.58	29.25	2.34	2.17	1.39
124	84.68	39.25	33.54	1.93	2.17	1.17
134	54.68	41.25	27.91	2.52	2.30	1.48
144	54.63	44.23	29.76	2.66	2.31	1.49
154	55.85	40.36	27.64	2.63	2.29	1.46
214						
224						
234	This series at this temperature was so soft that it was impossible to handle the specimens.					
244						
254						
264						
314	8.55	53.47	26.37	4.36	2.22	2.03
414	61.19	50.46	37.25	2.73	2.22	1.35
424	55.23	48.24	33.79	2.76	2.24	1.43
434	51.43	44.30	29.72	2.68	2.27	1.49
444	52.45	39.27	25.33	2.55	2.38	1.55
454	47.82	40.84	26.35	2.62	2.31	1.55
464	50.59	38.25	24.72	2.50	2.35	1.55
514	56.38	50.99	37.10	2.80	2.16	1.37
524	58.64	53.02	38.62	2.92	2.19	1.37
534	59.19	48.67	36.15	2.62	2.15	1.35
544	57.01	48.27	35.18	2.71	2.16	1.37
554	51.77	47.71	33.41	2.69	2.18	1.43
564	52.21	47.82	34.09	2.69	2.19	1.40

TABLE V

TIGHTEST PACKING USING 35-MESH AND 100-MESH RAW KYANITE

Percentage		Volume Occupied	Time For Constant Volume min.
35-Mesh	100-Mesh		
100	0	5.79	18
90	10	5.41	14
80	20	5.30	16
70	30	4.98	16
60	40	4.79	17
50	50	4.95	16
40	60	4.91	17
30	70	5.25	18
20	80	5.36	20
10.	90	5.53	16
0	100	5.88	18

TABLE VI

TIGHTEST PACKING USING 35-MESH AND 100-MESH CALCINED KYANITE

Percentage 35-Mesh	Percentage 100-Mesh	Volume Occupied	Time For Constant Volume min.
100	0	7.04	15.0
90	10	6.60	17.5
80	20	6.06	15.0
70	30	5.60	15.0
60	40	5.23	15.0
50	50	4.95	15.0
40	60	4.92	15.0
30	70	5.05	15.0
20	80	5.04	15.0
10	90	5.45	15.0
0	100	5.19	15.0

TABLE VII

CHEMICAL ANALYSIS*

Standard Raw Kyanite

Al_2O_3	58.77%
SiO_2	37.70
Fe_2O_3	1.17
TiO_2	1.30
MgO	trace
K_2O and Na_2O	0.59
Ignition Loss	0.38
	99.91%

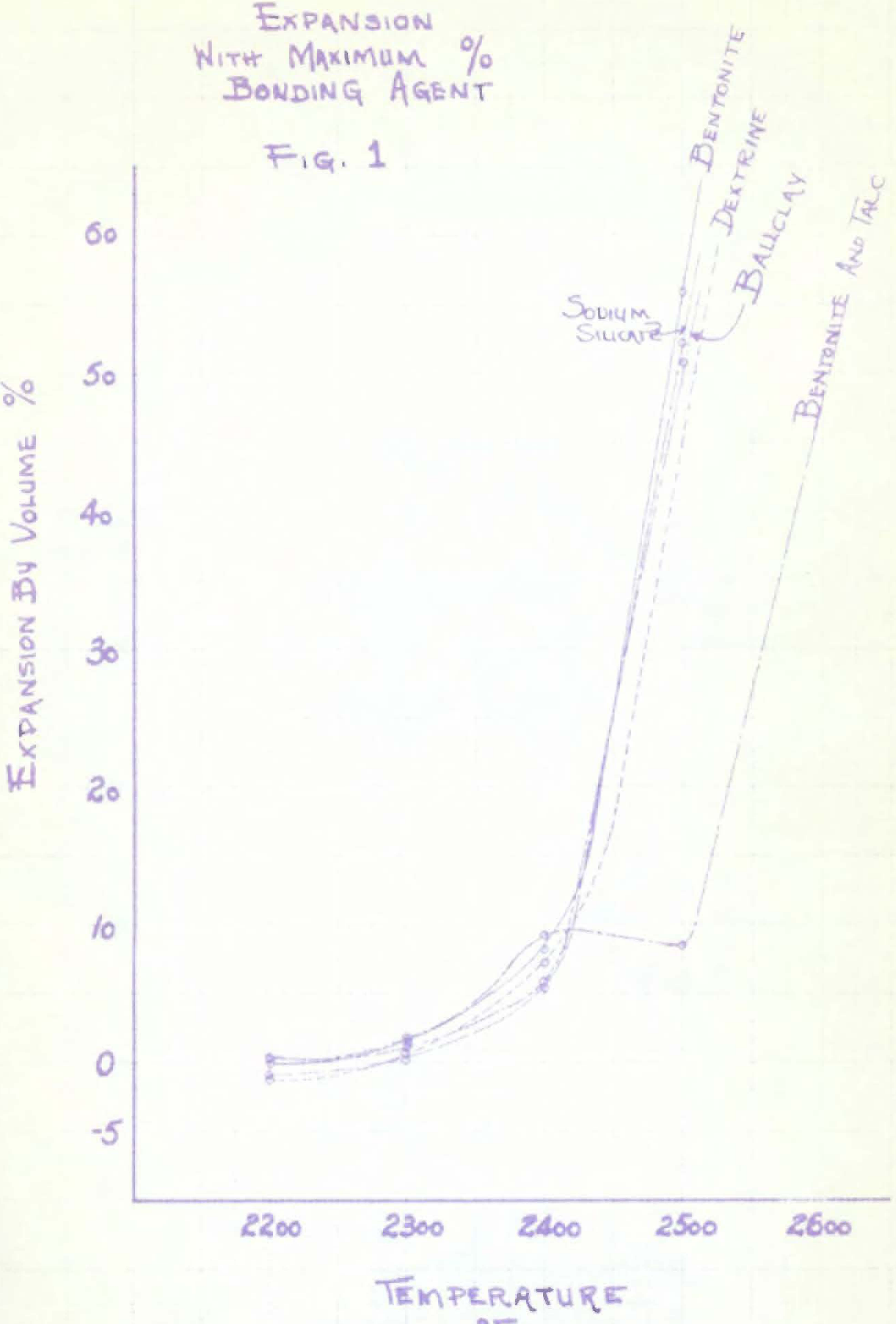
Acid-Washed Raw Kyanite

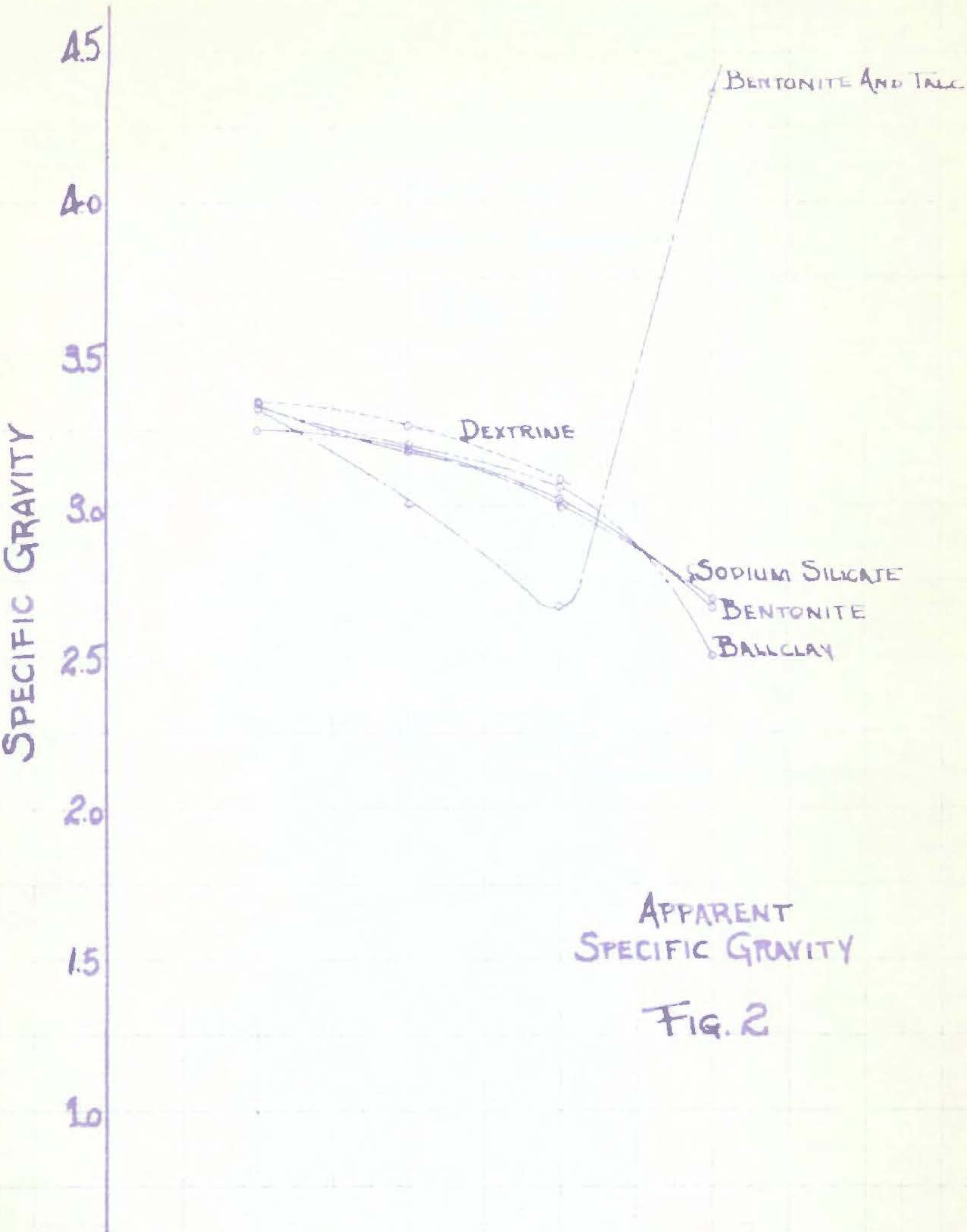
Al_2O_3	59.13%
SiO_2	38.20
Fe_2O_3	0.42
TiO_2	1.20
MgO	trace
K_2O and Na_2O	0.49
Ignition Loss	0.48
	99.92%

*Supplied by Phosphate Recovery Corporation

EXPANSION WITH MAXIMUM % BONDING AGENT

FIG. 1



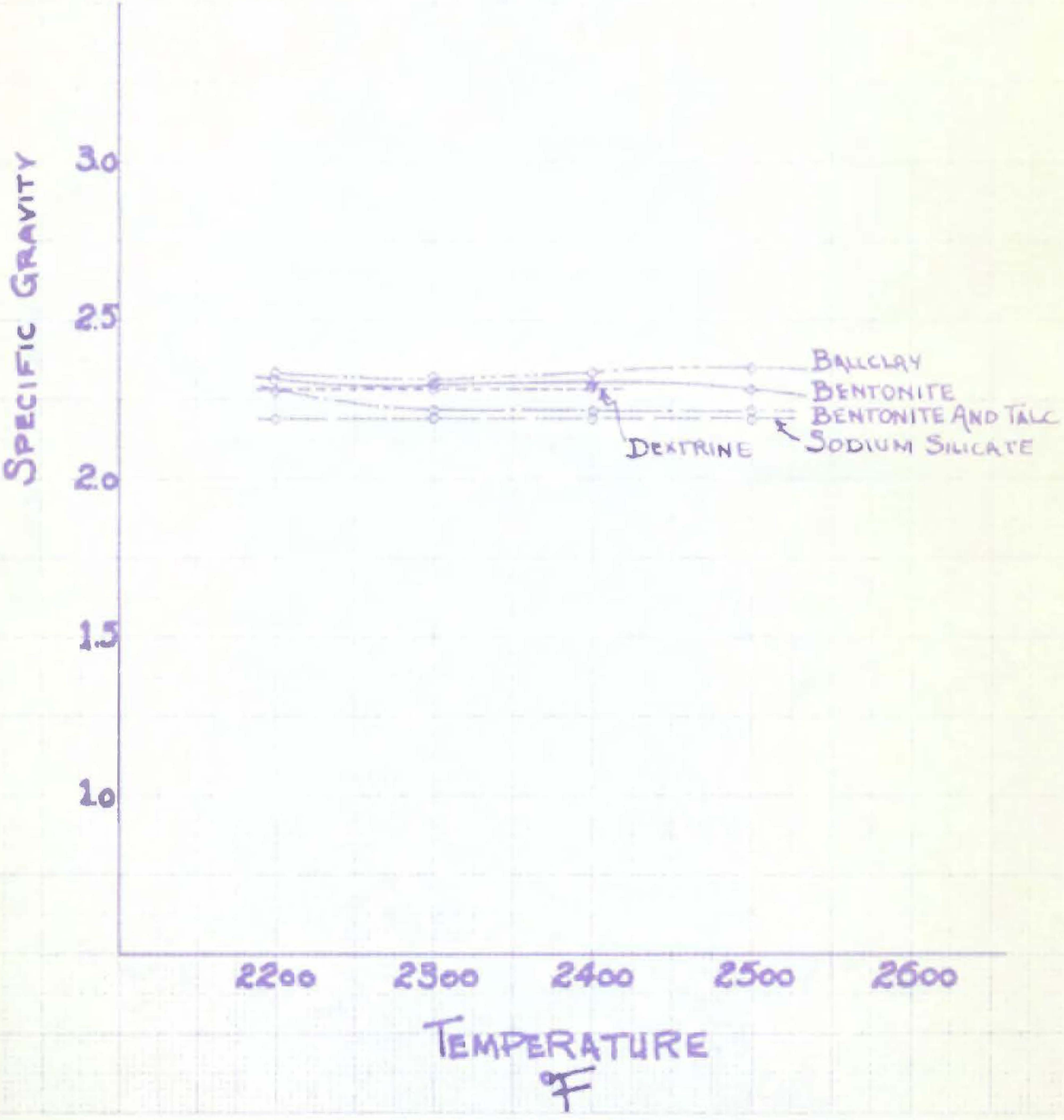


APPARENT
SPECIFIC GRAVITY

FIG. 2

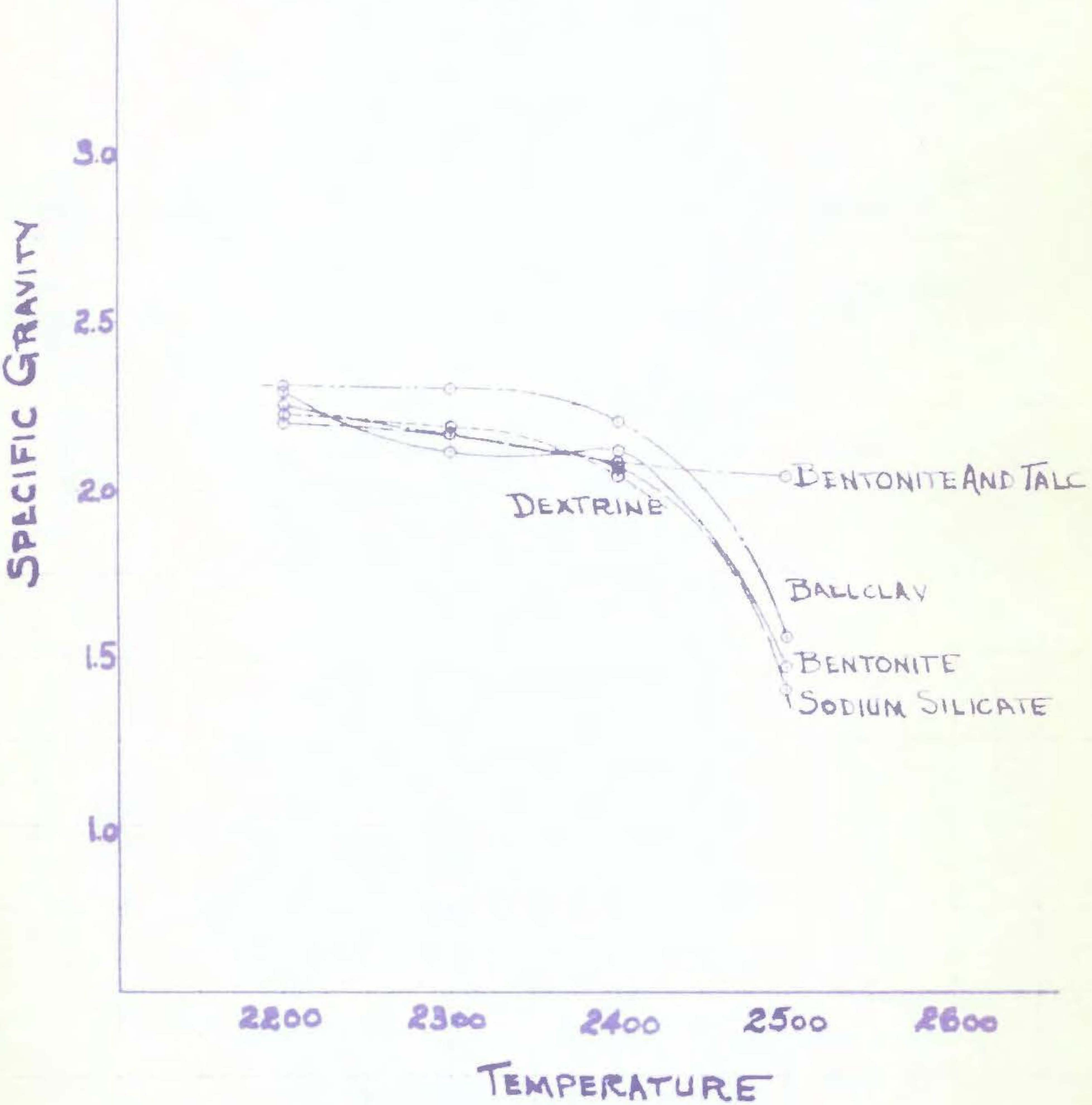
DRY BULK
SPECIFIC GRAVITY

FIG. 3



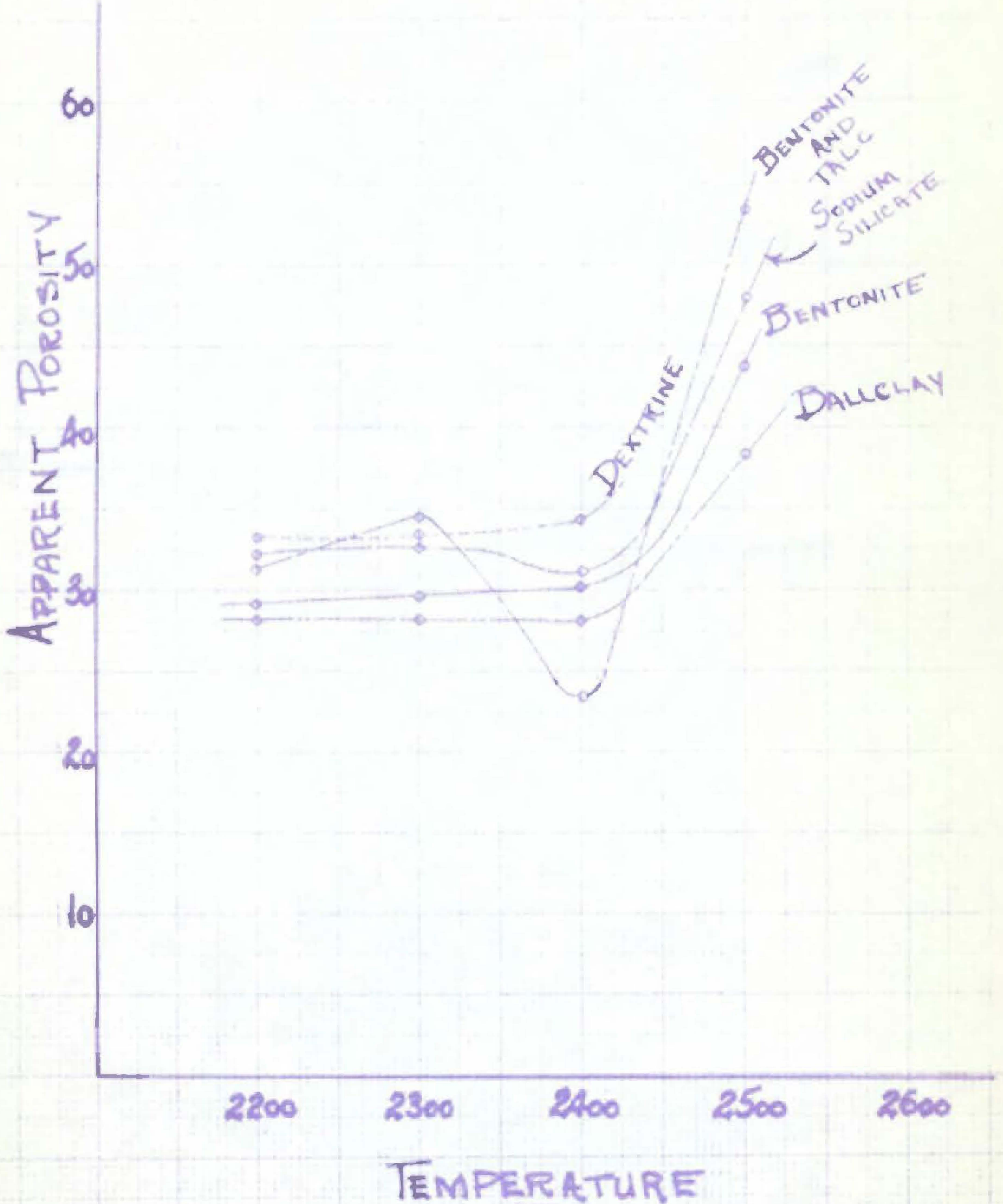
FIRED BULK
SPECIFIC GRAVITY

FIG. 4



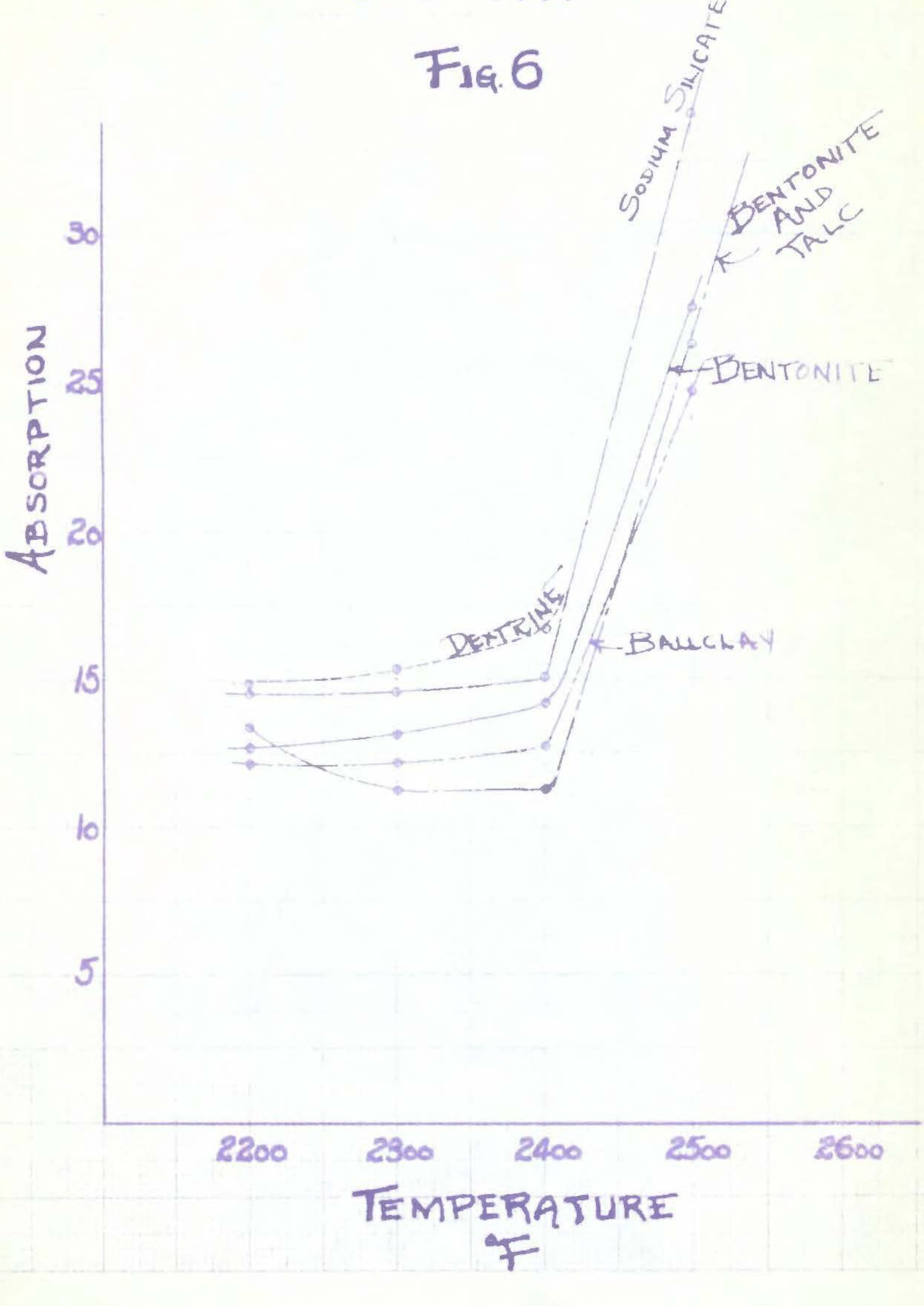
APPARENT POROSITY
USING THE MAXIMUM %
BONDING AGENTS

FIG. 5



ABSORPTION
Using The Maximum
Bonding Agent

Fig. 6



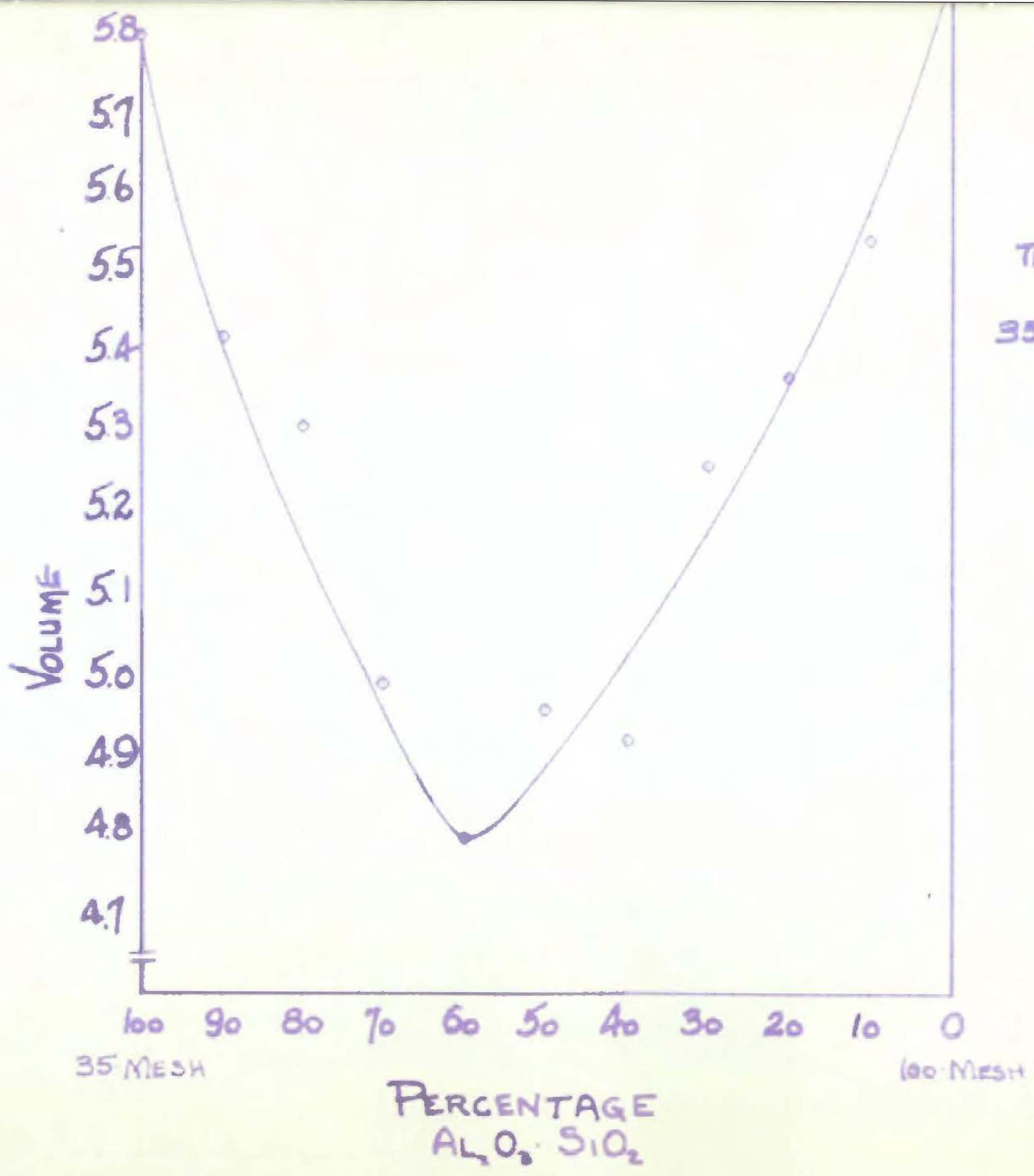


Fig. 7

TIGHTEST PACKING
OF
35-MESH AND 100-MESH
RAW KYANITE

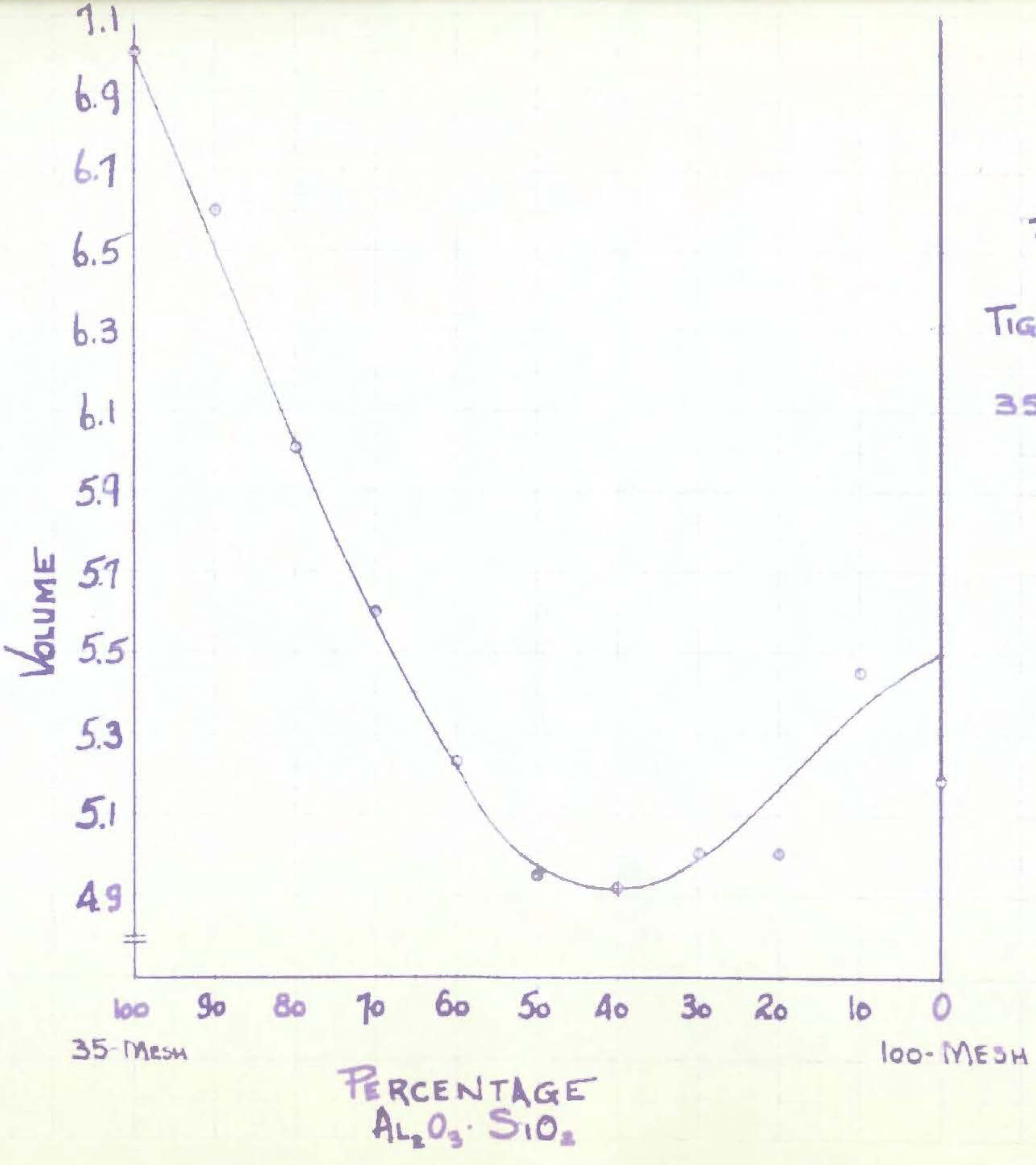
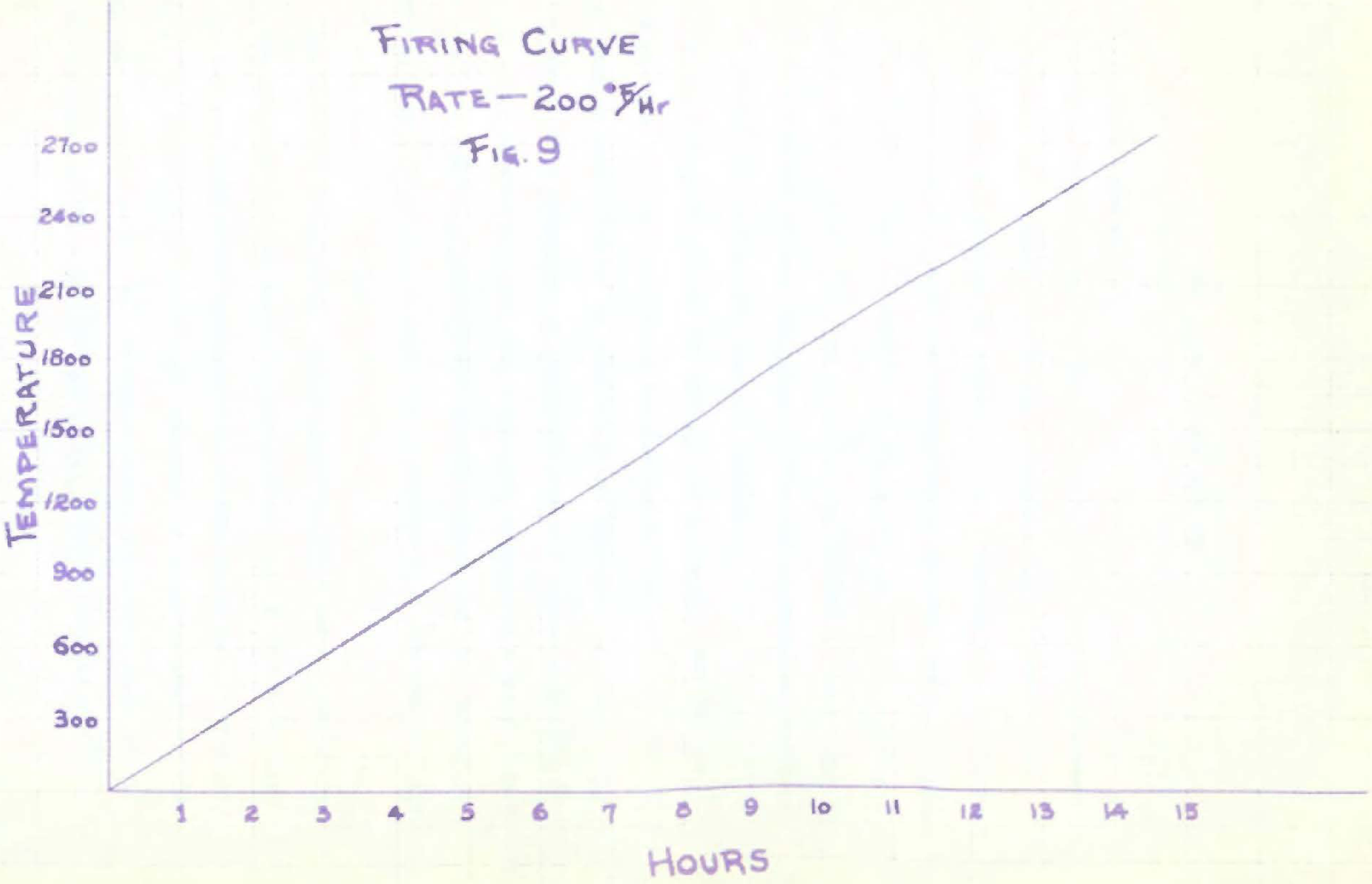


Fig. 8

Tightest Packing
of
35-Mesh and 100-Mesh
Calcined Kyanite



FIRING CURVE
RATE — 200°F/Hr
FIG. 9

V. DISCUSSION OF THE RESULTS

Effect of Bonding Agents

Through a graphical presentation of the data, the effect produced by the bonding agents used aids in the interpretation of these data. The values which are plotted as points in Fig. 1 through Fig. 6 represent the data obtained when the maximum percentage of bonding agent is used. There are no points shown at 2600°F. as the specimens in all cases had expanded to such a state that they could not be handled. This is the result of insufficient interstitial glass formation and complete decomposition of the kyanite grains into mullite crystals.

The bonding agent giving the most favorable results and the one which was used in later work was a combination of bentonite and talc. The other bonding agents failed to show any glass formation at higher temperatures, while the combination of bentonite and talc showed a decided development of glass at 2500°F. This point is shown in Figures 2 and 4. In mixing the batches a perfectly homogeneous body is desired and this factor is shown by Figure 3 which is a graphical presentation of the dry bulk specific gravity.

The apparent porosity and absorption, Figures 5 and 6, have a sharp increase after 2400°F. is passed. This is explained by the large expahsion which accompanies the decomposition of kyanite to mullite and the lack of the formation of sufficient interstitial glass to overcome this expansion. Bentonite and talc mixtures showed the formation of glass within the body by the sharp decline of the porosity line at 2400°F.

The effect of bentonite and talc mixtures is explained by their pyrochemical behavior at higher temperatures. Bentonite is a highly colloidal material and serves as an excellent bonding agent in the dry state. Talc becomes advantageous as a flux at high temperatures causing the bentonite to produce a glass at a lower temperature. The effect of glass formation is shown by a higher apparent specific gravity and a delayed expansion.

Behavior on Heat Treatment

Although Peck[24] found that pure kyahite when heated to about Cone 12 (1310°C.) decomposes into mullite, $3Al_2O_3.2SiO_2$, and silica, SiO_2, it was found that the decomposition of this Virginia kyanite becomes evident at Cone 14 (1400°C.) and is complete at Cone 15 (1435°C.). As a result of heating to these temperatures, the Virginia kyanite becomes white and granular. However, there is the appearance of a very small percentage of dark particles in the concentrate which is due to the presence of accessory minerals.

During the decomposition range from Cone 14 to 15, the expansion of kyanite is very sharp and its increase in volume is shown by the decrease in specific gravity. The change is from approximately 3.5 to 2.9. The rate of linear expansion of kyanite increases with the temperature and with the fineness of the grain. When the grain size is reduced to 200-mesh and finer, however, the percentage of the volume or linear change is not as great as in the case of grain sizes larger than 200-mesh.

The effect of the heat treatment may be noted from the photomicrographs of Figure 10 and Figure 11.

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[24] A. B. Peck, "Changes in the Constitution and Microstructure of Andalusite, Kyanite, and Sillimanite at High Temperatures and Their Significance in Industrial Practice", Jour. Amer. Ceram. Soc., 8, 7, 407-29 (1925).

Fig. 10
Raw Kyanite, crossed nicols,
tint plate, 144X

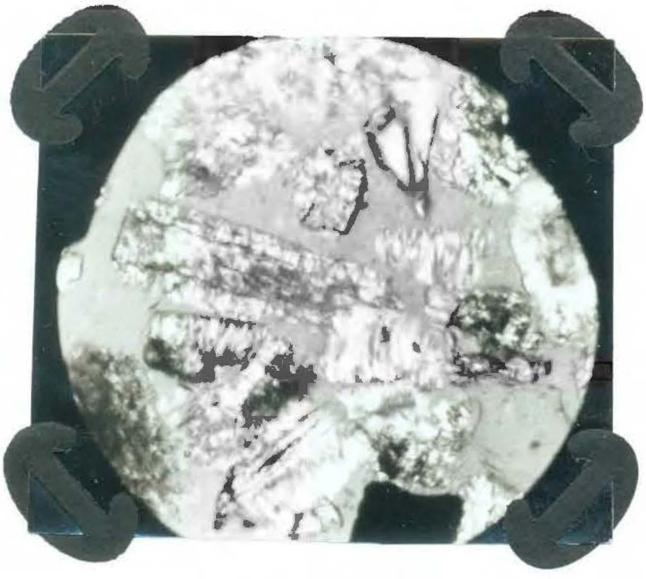

Fig. 11
Calcined Kyanite
at 1435°C, crossed nicols,
tint plate, 144X

Figure 10 shows the crystals of raw kyanite with the characteristic bladed or shaft-like structure. The decomposition of the kyanite crystals into mullite and silica is shown in Figure 11. The larger crystals are those which just pass a 100-mesh sieve. Comparing Figure 10 and 11, the effect of calcination is shown. The typical kyanite crystals have been thoroughly "shot-through" by needle-like crystals of mullite.

By using calcined kyanite as a source of introducing mullite into a body, about 87.5 parts of mullite are introduced for each 100 parts of calcined kyahite. Most of the remainder is silica which was liberated by the decomposition of the kyanite. This percentage of mullite is based on the percentage of alumina present in the kyanite and on the specific gravity of the resulting compounds. Pure mullite has a specific gravity of 3.03 and the specific gravity of calcined kyanite is approximately 2.92 to 2.96. Assuming that a mean of the specific gravities of tridymite and cristobalite is 2.25, as the amount of each is not known, it was found that approximately 2.93 is the specific gravity of calcined kyanite, having as complete a decomposition to mullite as is possible. The rutile and heavy minerals present in the unconverted state tend to alter slightly the above calculations. This is the reason that the specific gravity of this calcined kyanite approaches that of the theoretical value.

Softening Point (P.C.E.)

A representative sample of the Virginia kyanite was made into pyrometric cones. These cones were subjected to the pyrometric cone equivalent (P.C.E.) test in the usual manner. Based on two trials, the softening point, expressed in terms of standard Orton cones, was 36 to 37. It was also found that the P.C.E. value of this kyanite was not greatly affected when compounded with small percentages of mineralizers and fluxes.

Grain Sizing

The percentages giving the tightest packing are 60 per cent 35-mesh raw kyanite and 40 per cent 100-mesh raw kyanite. The results of a similar test using calcined kyanite showed that 40 per cent 35-mesh calcined kyanite and 60 per cent 100-mesh calcined kyanite produced the tightest packing.

Only raw kyanite was used in this investigation because of the desire of the sponsor of this work. The results of using a tightest-packing mixture did not prove successful in forming a compact, dense body with the percentage of bonding agents and pressure used. It did, however, lead to the reduction of the grain size and a higher forming pressure in later work, the percentage of the bonding agents being held constant.

Petrographic Examination

A petrographic examination of samples of raw kyanite, tightest pack of 35-mesh and 100-mesh, was made on powdered samples which were made to pass through a 100-mesh sieve and were retained on a 200-mesh sieve. The samples fired to 2200°F. and 2300°F. showed no noticeable evidence of any decomposition. An examination of the kyanite samples fired to 2400°F. gave evidence of a slight decomposition of the kyanite to mullite on the edges of the smaller grains. This is typical of the manner in which mullite crystals begin to form. Greig[25] found this to be true in making a study of the formation of mullite from kyanite, andalusite, and sillimanite. At 2500°F., the decomposition of kyanite to mullite has proceeded to a high degree. There is evidence of some free quartz which has not been appreciably affected by the heat treatment; however, there is

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[25] J. W. Greig, "Formation of Mullite from Kyanite, Andalusite, and Sillimanite", Jour. Amer. Ceram. Soc., 8, 8, 465-83 (1925).

some tridymite and/or cristobalite. At 2600°F., there has been a maximum decomposition of the kyanite grains to mullite and silica. The grains of kyanite have been totally decomposed and now these grains are "shot-through" with the needle-like crystals of mullite. The molecule of silica which is liberated with the formation of each molecule of mullite has taken the form of tridymite, cristobalite and/or glass.

Spectrographic Examination

A qualitative spectrographic examination of the Virginia kyanite revealed that a small part of a per cent of chromium, silver, and zirconium was present. The spectrograph is of advantage in determining very small percentages of an element and those mentioned above are not present in amounts greater than 0.2 per cent and some in less than 0.1 per cent. This is the reason the compounds of higher percentages are not noted here; however, they do appear in the spectrum of kyanite.

Supplement to Petrographic Examination

In determining the state of the iron present, it was found that rutile is present, perhaps containing iron in solid solution. Limonite is present adhering to the grains of kyanite. There are also remaining in the samples sent to the laboratory, particles which are magnetic. There is possibly some small amount of hematite present.

VI. CONCLUSIONS

The results of this investigation agree with the work of Harrison[26] who found by specific gravity determinations that time is not so vital a factor as temperature in governing the rate of decomposition of kyanite, above the initial reaction temperature. At 2600°F., there has been total decomposition of the kyanite grains into mullite crystals.

The results obtained indicate that to secure a compact, dense structure in a body using at least 96 per cent raw kyanite, an increase in the forming pressure and a reduction in the grain size are necessary.

The introduction of small percentages of mineralizers and fluxes into the body does not greatly affect the softening point of the fired mixtures.

Small percentages of bentonite and talc gave the best results and were used in later work in compounding a dense, compact body using high percentages of raw kyanite.

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[26] H. C. Harrison, "Kyanite-Clay Refractories - I", Jour. Amer. Ceram. Soc., 9, 5, 257-71 (1926).

VII. ACKNOWLEDGEMENT

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