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Bhikhubhai Mahadeo Sedalia

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BAUXITE VERSUS DIASPORE CLAY IN
HIGH ALUMINA (70%) REFRACTORY BRICK

BY

B. M. SEDALIA

A

THESIS

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Approved by - Paul G. Herold
Professor of Ceramic Engineering

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INTRODUCTION

The last twenty five years have seen a remarkable change in the character and types of refractories for furnace construction. Not much more than a few years ago, the production of refractories consisted almost solely of fireclay and silica shapes. A few high alumina bricks were made from Missouri diaspore clays or from bauxite and fire clays. At a later date, although little used, high alumina refractories were available which were made from alumina of a higher degree of purity, by the fusion process. Today refractories covering the entire range of composition from about 98% SiO_2 to 99 1/2% Al_2O_3, except for a short interval from about 4 to 12% Al_2O_3, are finding wide commercial applications.

High alumina refractories are those having an alumina content of 50% or higher with the remainder being essentially silica, and are arbitrarily divided into three groups depending upon alumina content. They are 50%, 60%, and 70% Al_2O_3 refractory bricks. Fused alumina refractories are grouped separately. To manufacture such high alumina refractories, raw materials high in alumina content such as diaspore clay and bauxite are mainly used. Naturally occuring alumina-silicate minerals like sillimanite, kyanite, and andalusite are also used for manufacturing high-alumina refractories or mullite refractories.

In this country, diaspore clay, since its discovery has remained the chief source of raw material of high alumina content. The deposits of diaspore clay of economically workable size are located only in the South Central Missouri district. This area being the only commercial source of diaspore clay, the refractory industries are alive to the fact that, at the present rate of consumption of diaspore clay, this source will be exhausted within a comparative short time. Greaves Walker (1) had pointed out this situation back in 1928, and suggested that other raw materials such as bauxite, kyanite, Georgia Kaolin may be substituted for diaspore clay.

As a result of this situation, the use of bauxite for manufacturing high alumina refractories is being seriously considered by the refractories industry. In the last few years the importation of gibbsite from Dutch, French or British Guiana, has supplied a very high grade of refractory material to make high alumina refractories in place of diaspore clay. Much effort is made now days to utilize this material.

Very recently some refractory manufacturers who have used Dutch Guiana gibbsite for making high alumina refractories, have experienced strange behaviors of such refractories toward reheat. They observe that their refractories show appreciable expansion when subjected to reheat tests. This is quite contrary to the general belief at present that bauxite refractories show continuous shrinkage on repeated firings. In light of such development this investigation was undertaken. This investigation is a comparative study of bauxite and diaspore clay when used to manufacture high alumina (70%) refractories. High alumina grog is prepared by calcining these raw materials at various temperatures, and bricks of 70% Al_2O_3 were made using this

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(1) A. Greaves Walker, 'After Diaspore - What?', Blast Furnace, Steel Plant, 16, 1481-82, (1928).

grog with plastic fireclay as the bond. These bricks are then subjected to various reheat temperatures and all changes in volume stability of the bricks are recorded. Finally an effort is made to explain the cause or causes of such expansion changes by x-ray diffraction investigation, and by other methods.

REVIEW OF LITERATURE

A survey of the literature for the present investigation, showed that not much work has been done on this problem. Much has been reported about diaspore clay, bauxites, high alumina refractories and other allied subjects and is briefly summarized as follows:

Since the discovery of diaspore clay, most high alumina bricks have been made from diaspore clay, and as a consequence, the high alumina refractories are designated as 'Alumina-Diaspore fireclay brick' by the A.S.T.M. (2). The 70% Alumina-Diaspore fireclay brick is defined by A.S.T.M. (2) as refractory brick having diaspore as an essential original ingredient, an alumina content of 70 ± 2.5% and a Pyrometric Cone Equivalent not lower than Cone No. 36 (3290°F).

Diaspore clay (3) is slightly plastic, light grey, buff or red in color and is generally of a rough, open textured porous nature, although dense rock-like samples are also known. The most striking feature of diaspore clay is the presence of oolites or shot like particles determined microscopically by Wherry and Ries (4) to be composed of the mineral diasporite which is the basis of the characteristic high alumina content. The oolitic particles occur in a porous ground mass of extremely fine grained clay. The theoretical composition of oolitic diasporite is $Al_2O_3 \cdot H_2O$ containing 85% Al_2O_3 and 15% combined water.

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(2) Manual C-8 of A.S.T.M. Standards on Refractory Materials, Feb. 1948 Edition published by Amer. Soc. for Testing Materials, Phila., Pa. Page 25.

(3) H.S.McQueen; Geologic relation of diaspore and flint fireclay of Mo.; J. Am. Ceram. Soc., <u>12</u>, 687-97 (1929)

(4) E.T. Wherry and H. Ries; Diasporite in Missouri; Am. Minerologist II, No. 12 (1917)

Commercial diaspore clay (5) is essentially a mixture of diasporite mineral and clay and may analyse between 65% to 75% Al_2O_3. Diaspore clay usually carries a maximum silica content of 10% or less and the percentage of this constituent determines the quality. Lime, magnesia and alkalies are variable and usually do not occur in large amounts. Like bauxites, diaspore clay has high TiO_2 content which ranges from 3 to 4%. Iron oxide seldom exceeds 2 to 3% in the commercial refractory grades. Some of the typical chemical analyses of diaspore clay from Missouri are given in the following table:

TABLE I

Chemical Analysis of Diaspore Clays (6)

	A	B	C	D
SiO_2	6.18%	6.0 %	2.86%	4.06%
Al_2O_3	72.54	72.67	77.0	75.32
Fe_2O_3	1.56	1.91	1.65	1.91
CaO	0.22	0.14	0.12	0.17
MgO	0.11	0.14	0.09	0.08
TiO_2	3.16	3.16	3.16	3.06
$Na_2O + K_2O$	1.34	1.03	0.62	1.24
Ignition Loss	16.22	16.38	16.58	16.30
	99.33	99.43	100.06	100.14

A - Diaspore clay, soft, fine grained variety
B - Diaspore clay, hard, very fine grained, rocklike variety
C - Diaspore clay, fairly hard fine grain variety
D - Diaspore clay, very porous, open texture variety

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(6) McQueen, H.S., and Herold, P.G., 'Fireclay Districts of East Central Missouri'. Mo. Geological Survey and Water Resources, Rolla, Mo. Vol. XXVIII. Second series, (1943).

Thermal Dissociation of Diaspore Clay

The study of thermal dissociation of diaspore clay and mineral changes taking place on account of heating has been determined by Herold and Dodd (7). They have shown that commercial diaspore clay on heating does not change materially up to 350°C. Between 350 and 400°C, there is a sudden destruction of diasporite to form corundum and γ-alumina. The formation of γ-alumina is relatively rapid up to a temperature of 550°C, when the formation of corundum becomes more rapid. This indicates that γ-alumina is being changed to corundum above 550°C. At 950°C the γ-alumina has been entirely converted to corundum and there is no further increase in corundum content. From 1058°C to 1200°C, mullite is forming from the combination of the free quartz and combined silica present in the clay fraction with the corundum.

As the corundum is being formed at 400°C, it apparently picks up traces of iron, chromium, vanadium and strontium which increases the molecular size of the corundum molecule. More of these materials are picked up in solid solution until at 750°C, a maximum increase is reached, which on further heating is gradually decreased. At 900°C, there is a sudden elimination of the elements mentioned by sublimation giving a reduction in size of the corundum molecule. These elements in the solid solution are not entirely eliminated up to 1700°C.

R. A. Heindl (8) has studied the effect of high temperature on diaspore clay. He reports that when diaspore clay is heated to 1400°C,

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(7) P.G.Herold and C.M.Dodd, Thermal dissociation of diaspore clay; J. Am. Ceram. Soc., 22, 388, (1939)

(8) Heindl, R.A., The thermal expansion of refractories to 1800°C; Bur. Standards, J. of Research. Res. Paper No. 562, 10, 715, (1938)

the mass is almost wholly corundum and glass. He does not indicate anything about mullite formation at this temperature, but states that when heated to 1720°C, corundum grains become much larger and mullite occurs as interstitial material associated with the glass.

As to suitability of diaspore clay for manufacturing high alumina refractories, its shrinkage has remained the main handicap. Constancy of volume in service is one of the many requisites of refractory materials. Such a property is most difficult to secure in diaspore refractories as the complete shrinkage of this clay is not obtained unless fired at high temperatures, which is a costly process.

Phelps (9,10) has made a study of such shrinkage of diaspore clay. He reports that the shrinkage of various types of diaspore clays under given conditions of time and temperature is inversely in the order of alumina content. The duration of firing is of great importance in causing the maximum shrinkage to take place. The state of division is also important in effecting the shrinkage. He also reports that great differences exist between the firing properties of the bond or the plastic portion, and the diasporite grains. Therefore he suggests that diaspore refractories should receive sufficient heat treatment during the manufacturing process to approximate a permanent volume. Otherwise shrinkage will occur in service by the affect of continued time or temperature. Phelps also reports data on development of methods which will shrink diaspore without firing to exceedingly high temperature for

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(9) Phelps, S.M., A Study of Shrinkage of diaspore clay; J. Am. Ceram. Soc., <u>9</u>, 659 (1926)

(10) Phelps, S.M., A Study of shrinkage of diaspore clay; J. Am. Ceram. Soc., <u>15</u>, 96 (1932)

long periods of time. Experimentally he has shown that this can be accomplished by a number of shrinkage producing materials. It is shown that these should be added in definite percentages and the greatest shrinking effect will be produced by fine grinding, high pressure moulding of calcined dobies and by firing to moderate temperature. Phosphate rock which is essentially tricalcium phosphate is most practical for preshrinking. Maximum shrinkage is produced when the dobies containing this material are fired to Cone 18 to 20.

Bauxite (11) has been assigned the chemical formula $Al_2O_3.2H_2O$, though essentially it is a mechanical mixture of both diasporite $Al_2O_3.H_2O$ and gibbsite $Al_2O_3.3H_2O$. Bauxite as it occurs in nature rarely exhibits the distinct characteristic of its constituent minerals. This becomes apparent only on the examination of thin sections under the microscope, by heating curves, by chemical analysis or by x-ray diffraction technique. Not all the constituents in bauxite are recognizable even by such methods and it is believed therefore that much alumina is present in the form of a colloidal hydrogell with a variable combined water content.

Bauxite is a medium soft to hard rock, having a cellular, porous, compact fine grained structure, a conchoidal or uneven fracture and ranges in color from light gray, cream, pink or yellow to dark brown and dark red. Bauxites are characterised by oolitic or pisolitic structure, the oolites ranging from 1/20'' to 1/2'' in diameter. The

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(11) Selley W. Mudd Series, Industrial Minerals & Rocks, p. 96 (1949) Amer. Inst. Mining & Met. Engs.

color of the oolites generally differs somewhat from that of the matrix, but are not much darker. The main coloring pigment is iron oxide though organic matter affects the surface ore, changing it to gray.

The common types of bauxite are designated as follows:

(1) Oolitic-pisolitic ore in which the nodules vary from microscopic size to 1'' or more in diameter.

(2) Amorphous ore mixed with some oolites.

(3) Sponge ore which is granular in character and presents the original structure of syenite from which it is formed due to weathering.

Pure bauxite would usually analyse as having 58 to 60% Al_2O_3, 3 to 6% SiO_2, 1 to 2% Fe_2O_3, 2 to 3% TiO_2 and about 30% combined water. Some chemical compositions of typical bauxites are given below.

TABLE II

Chemical Analysis of Bauxites

	A	B	C	D
SiO_2	11.48	2.0	26.0	4.5
Al_2O_3	57.62	62.05	54.0	58.4
Fe_2O_3	1.83	1.66	1.0	3.2
CaO	-	-	-	0.4
MgO	-	-	-	-
TiO_2	-	3.50	2.1	3.2
Ignition Loss	28.63	30.31	16.1	30.6
	99.56	99.52	99.2	100.3

A - Arkansas bauxite (12), Gray variety
B - Arkansas bauxite (12), Pink variety
C - Georgia bauxite (13).
D - Dutch Guiana bauxite (13).

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(12) Branner, G.C., 'Outline of Arkansas Mineral Resources', published by B. of Mines, Manufacture and Agricultural and State Geological Survey. Little Rock, (1927), pp. 69.

(13) F.H.Norton, 'Refractories', 3rd edition, McGraw-Hill Book Co., (1949) p. 44.

The Dutch Guiana bauxite used for this investigation is a most pure form of bauxite and serves the purpose of supplying a high grade of refractory material for manufacturing high alumina refractories.

Norton (14) carried out the thermal analysis of this bauxite and determined its mineral composition. This Dutch Guiana bauxite consists of 88% gibbsite, 6% diasporite and 6% kaolinite. Hence, it is evident that it is mostly in the form of gibbsite. The chemical analysis has been reported as D of Table II.

The British and French bauxites (15) are also pure forms of bauxites and are close to the chemical composition of Dutch Guiana bauxite.

Action of heat on gibbsite and bauxite

Rooksby (16) made an x-ray examination of the action of heat on $Al_2O_3.3H_2O$, the trihydrate of alumina. This is the mineral gibbsite. As there is no literature reported on the actual action of heat on bauxite, the results obtained by Rooksby will closely fit Dutch Guiana bauxite. He reports that when trihydrate of alumina viz. gibbsite, is heated to 200°C, a definite hydrate $Al_2O_3.H_2O$ is formed. Though the chemical formula for this hydrate is that of the mineral diasporite, the x-ray pattern is much different from diaspore, but there is little resemblance to the bauxite patterns.

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(14) F.H.Norton, Thermal analysis of high alumina clays by thermal methods, J. Am. Ceram. Soc. 23, 281, (1940)

(15) Emory, L.T., British Guiana bauxite deposits, Mining & Met., 9, 8, (1928).

(16) H.P.Rooksby, An x-ray examination of the effect of heat on aluminum hydroxide - $Al_2O_3.3H_2O$, Trans. Brit. Ceram. Soc. 28, 399, (1929).

Between 250°C and 500°C, the hydrate $Al_2O_3.H_2O$ loses water completely with formation of γ-alumina. The x-ray pattern consists of sharp lines, and the growth of γ-alumina crystals take place between 500°C and 950°C. At 1000°C, γ-alumina begins to change to corundum or α-alumina. On further heating, this change to corundum is completed at 1150°C. As this is just for the pure material it does not give any account of the effects produced by impurities present in bauxite or gibbsitic bauxite.

Heindl (17) has examined the commercial bauxites at much higher temperatures. He reports that bauxite when heated to 1400°C, principally contains corundum with lesser amounts of mullite, glass and a compound of what is probably Fe_2O_3 and TiO_2. On further heating to 1690°C, it is not greatly changed from the preceding stage, except that the size of mullite crystals is increased and the crystals of corundum show evidences of reaction with the fluxes present.

Effect of Calcination on Clays.

Either bauxite or diaspore when required for use in refractory manufacture, must be calcined so that the characteristic shrinkage of the material may be removed. As previously stated, Phelps (18) has suggested some methods by which the shrinkage of diaspore clay can be completely removed by the use of phosphate rock. No such work has been reported for bauxite. Riddle (19) has made a study of

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(17) R. A. Heindl, Op. Cit.

(18) Phelps, S.M., Op. Cit.

(19) F. H. Riddle, The effect of preparation and calcination treatment on the properties of the kaolin-alumina mixtures. J. Am. Ceram. Soc., 15, 583, (1932).

calcination treatment of kaolin-alumina mixtures. He used many kaolinitic clays mixed with bauxite clay. As to the effect of calcination at various temperatures, he reports that at about 1200°C these clays dissociate into mullite and cristoballite. As the temperature increases, the cristoballite combines with the alumina already present to form increased amounts of mullite. He shows this in an x-ray diffraction study in which the cristoballite lines grow weaker, as do the alumina lines, but simultaneously the mullite lines grow stronger, at the same time some of the cristoballite probably combines with small amounts of alkali and alkaline earths present in the clay to form glass.

He summarizes his findings as follows:

(1) The calcines fired at Cone 16 showed free corundum and those fired at lower temperatures showed much more free corundum.
(2) None of the calcines showed any uncombined clay. All the clay has either dissociated into aggregates of mullite crystals and glass, or at least part of the excess SiO_2 glass formed by dissociation has combined with some of free alumina or corundum to form additional mullite.
(3) Free corundum is present in all calcines in varying amounts including those fired at Cone 20.
(4) The effect of grinding is very marked on calcination. There is increased combination of corundum to form more mullite and it is more pronounced on fine grinding.
(5) The glass in the calcines contains exceedingly fine crystals of cristoballite.

Mineral Changes Taking Place During Firing Operation of Refractories

The literature survey thus far has covered the effect of calcination of clays, diaspore and bauxite. Consideration will now be given to mineral changes during the firing of fire clay refractories. As far as the clay, or diaspore constituent of a refractory is concerned the behavior is the same as was described for individual clays.

But up to this point little has been said regarding the effects of the accessory minerals at high temperatures. Some of the oxides other than silica and alumina lower the temperature at which the liquid begins to form and increase the amount of liquid at any given temperature.

The alkalies (soda and potash) are especially potent, reacting to form a highly viscous liquid at several hundred degrees below the temperature at which liquid would begin to form if the mixture consisted wholly of alumina and silica. In this alkali-alumina-silica liquid, accessory minerals containing lime, magnesia and iron would dissolve wholly or in part as would both amorphous and crystalline silica; and at very high temperatures even mullite would dissolve. So the temperature of liquid formation would therefore depend upon the alumina-silica ration, and upon the compositions and amounts of the accessory minerals.

When fireclay refractories are cooled from the firing temperatures, some crystalline material especially cristoballite and mullite may separate from the liquid. However, much of the liquid cools to a rigid glass, which bonds the mass together and gives strength. Additional strength is imported by interlacing and adhering of crystals.

Fired high alumina bricks would contain mullite, usually corundum free silica and glass, in amounts varying with alumina content of the brick, the raw materials from which they were made, the proportion of accessory oxides and the firing treatment to which the bricks were subjected. If complete equilibrium could be attained during the firing, any pure alumina-silica refractory with less than 71.8% alumina would contain no crystalline material other than mullite and free silica. With more than 71.8% alumina, they would contain only mullite and corundum. However, in the bricks made wholly or in part from diaspore clay, corundum may be present even in the compositions with less than 71.8% alumina, and free silica may be present even in compositions with more than 71.8% alumina. Under favorable conditions the development of mullite during firing proceeds to an advanced degree, yet it does not proceed to completion. The mullite formed at the faces of the grains of diaspore appears to act as a protective film, retarding or preventing further reaction between corundum of the interior of the grain and the free silica formed from the fire clay between the grains.

Reversible and Irreversible Expansion of Refractories

Refractory (20) materials expand when heated. If, on cooling to the initial temperature, the volume of the material is exactly the same as that prior to heating the refractory is said to have expanded in a reversible manner. On heating beyond a definite temperature, however, many refractories exhibit a permanent contraction or expansion in volume, the final volume at room temperature no longer coinciding with the original one. Such expansion or contraction is of irreversible nature. The temperature at which the material begins to show changes in volume depend upon texture, firing temperature and chemical

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(20) G.R. Rigby, Reversible Thermal expansion of refractory material, Tran. Ceram. Soc. Brit. 37, 9, 355 (1938).

composition.

The reversible thermal expansion may be measured by direct or indirect methods. In the direct method the bar is heated in the furnace and the expansion of the material between two marks on the bar is obtained by direct measurement. The main advantages of this method is (1) large specimens can be used such as whole bricks, and (2) no previous calibration is necessary.

In the indirect methods of measuring the thermal expansion, the movement of the test piece is conveyed to the measuring mechanism by means of an intermediate substance. These indirect methods may be classfied according to the measuring device used. Such measurements are done by means of (1) dial gauge, (2) a micrometer microscope, (3) an optical lever, (4) a mechanical lever (5) interferometer, (6) silica glass dilatometer method and other miscellaneous methods of measurement. Rigby (21) has explained all such methods in detail to which the reader is referred.

Physical effects such as methods of manufacturing and variation in texture, grain size distribution greatly influence the thermal expansion of refractories. The coefficient of expansion is decreased with increase in apparent porosity and some cases is increased with increase in porosity. Such effects are produced during firing of bodies made by different forming methods.

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(21) G. R. Rigby, Op. Cit.

Loomis (22) has made an extensive study of porosity and volume changes of fire bricks at higher temperature. Porosity and change in volume of refractory has been shown by him to be a measure of the refractoriness. A decrease in porosity and volume indicates the progress toward vitrification and when these changes are plotted in the form of curves, the slope of the curves show the rate of vitrification. Overfiring is indicated by an increase in porosity or by an increase in volume as the vesicular structure accompanying overfiring is developed. He also relates the porosity change in a refractory with its load bearing capacity at elevated temperatures.

It was noted previously that when refractories are subjected to higher temperatures, an expansion or shrinkage of a permanent nature takes place, and when they are cooled they do not regain the original size. So this type of irreversible change in dimension is known as after-expansion or shrinkage. Sometimes the term 'Secondary Expansion' is also used.

After-shrinkage can easily be explained. Such changes take place only in cases when the brick had not been fired high enough or had not been held long enough at the high temperature. Sometimes when the liquid phase starts forming due to high temperatures, the pores are filled and the refractory shows shrinkage of a permanent nature.

Permanent expansion (23) at high temperatures is more difficult

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(22) G. A. Loomis, Porosity and Volume Change of clay firebricks at furnace temperature; Bur. Std. Tech. Paper No. 159. April, 1920.

(23) F. H. Norton, 'Refractories', 3rd edition, McGraw Hill Book Co.

to interpret than shrinkage. It may result from any of the following conditions:

(1) Transformations or reactions in the crystalline phases during firing, yielding products of lower true density than the reactants:- Underburned silica brick for example may expand considerably at elevated temperatures as a result of transformation of more quartz to cristoballite or tridymite. Certain bricks made of calcined diaspore and fireclay show a permanent expansion which is attributed to additional formation of mullite. This mullite forms by reaction of particles of calcined diaspore with silica from clay.

(2) Opening of lamination of clays:- This was investigated by Everhart (24) who concluded that the increase in bulk volume is caused by the opening natural laminations or bedding planes in the clay grains. This is characteristic of many clay deposits. When such clay is used for refractory manufacture, it would definitely show an expansion of permanent nature.

(3) Due to overfiring:- When certain clays (25) are heated beyond a critical temperature, they tend to swell and become vesicular, causing an expansion.

A.S.T.M. Reheat Test

Determination of the amount of changes in the dimension of refractory brick which may occur at high temperature is made by the

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(24) J.O. Everhart, Secondary expansion in refractory clays, J. Am. Ceram. Soc., 20, 353-59, (1937)

(25) J. L. Hall, Secondary expansion of high alumina refractories, J. Am. Ceram. Soc., 24, 349, (1941).

reheat test C-113-46 described by the American Society for Testing materials. (26) The reheat test is used to determine the effect of refiring, volume stability, and the extent to which the refractory has been previously fired.

In 1936, committee C-8 of A.S.T.M. proposed test procedure C-113 which specified that full 9'' x 4 1/2'' x 2 1/2'' brick be subjected to a temperature of 1400°C for 5 hours and the change in length determined. Before adopting C-113 as a tentative standard, extensive reheating tests at 1400°C were conducted. Procedure C-113 became standard in 1936 and since that time has received general approval as a control test as well as a specification test for standard fireclay brick. This test was then designated as C-113-36 for reheat change of refractory brick. This was further revised in 1946 and since then it is designated as C-113-46.

In the reheat test, the sample bricks are placed on the dummy bricks in the furnace. The furnace is gradually heated according to the schedule prescribed for the type of brick, and the furnace is held at that temperature for 5 hours. The furnace is then gradually cooled down. After cooling measurements are made on the test bricks and any change in linear dimensions is determined. These measurements are made to the nearest 0.02'' and all the percentages are calculated on the basis of the original length of the test brick.

E. C. Petrie and Walters (27) have subjected various refractories

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(26) Manual of A.S.T.M. Standards on Refractory Materials, (1948), p. 66.

(27) E. C. Petrie and Charles P. Walters, Reheat tests on fireclay and silica refractories, Bull. Am. Ceram. Soc., 23, 464, (1944).

to the reheat test and have studied the changes in various properties of the bricks as a result of the high temperature. They conclude that (1) The standard reheat test will not point out underfired first quality firebrick if the product exhibits the property of secondary expansion. Additional tests will be required to determine whether this is true of brick that do not show this expansion. (2) With first quality brick showing secondary expansion, those made by the stiff mud deaired process will show the greatest expansion, handmade somewhat less and the dry press least. Brick of harder burn will show less expansion than those of lighter burn. (3) First quality and super duty brick after the standard reheat test, assume almost identical properties irrespective of original firing temperature. (4) Underfired super duty brick showing no secondary expansion may sometimes be pointed out by the reheat test but not always.

U. S. Navy Simulative Service Test

Another test (28) that determines the after shrinkage or expansion of the brick is the simulative service test used by the U. S. Navy. It consists in building up two walls of a furnace, one of the brick to be tested and the other of a standard brick. The furnace is then run for 24 hours at a temperature of 1590°C and again at 1650°C, with an examination of walls between tests. An examination of the wall after it is cooled will indicate by the width of the open joints the

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(28) F. H. Norton, 'Refractories', op. cit.

approximate shrinkage of the bricks. This test is not quantitative but it does indicate reaction to service conditions. It is believed that a wall which shrinks a small amount at each joint is better than a wall which concentrates its shrinkage into a few large cracks. It might be remembered that such open joints may be substantially tight when at high temperatures.

Tredenick, Kelly and Burt (29) carried out repeated reheat tests on various grades of refractory and noted that the volume stability of firebricks is not always predictable from the results of reheat tests. The shrinkage or expansion on completion of the panel reheat test do indicate volume stability but do not always agree with permanent volume change results. From their observation of changes taking place after repeated reheat tests, they divide refractories into four categories according to behavior; (1) those showing shrinkage on repeated reheat, (2) those showing expansion after first reheat but shrinkage on repeated reheats, (3) those showing expansion after the first reheat and additional expansion on repeated reheat, and (4) those showing little or no change after the first reheat test.

They conclude that repeated reheat tests would give a better indication of volume stability of firebrick when in service than the present method of test.

Methods for Controlling Reheat Volume Change of Refractories

The major problem with which the high alumina refractory

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(29) Tredenick, W.T., J.F. Kelly, R.C. Burt; Comparison of repeated reheat tests of various grades of firebricks with service results; J. Am. Ceram. Soc., 29, 75, (1946).

manufacturer is confronted is the prevention of shrinkage, when such products are subjected to high temperatures during subsequent use. This after shrinkage is more important than after expansion as after expansion may be easily tolerated for bricks which are to be used in arches and walls. The most commonly known method for controlling such after expansion or shrinkage is to fire the refractories at somewhat higher temperatures than encountered in service. The grog or calcined clay also may be effectively used, but the main disadvantage is the undesired service contraction when actually put into service, after a period of time.

Vachuska and Bole (30) used a mixture of diaspore and kyanite for making high alumina refractories. Refractories made out of certain proportion of diaspore and kyanite showed practically no volume change due to heat treatment. The reason may be that there are two separate systems in metastable equilibrium, the one with the other. The first one is kyanite dissociating into mullite and silica glass and the second, the diaspore clay being converted to mullite and α or β - alumina. Thus shrinkage of diaspore is counter-balanced by the expansion of kyanite due to formation of mullite and silica glass. They also suggest that precalcination of the diaspore largely overcomes the shrinkage of the bricks of which it is a constituent. The higher the temperature of calcination, the higher can be the temperature to which the bricks may be subjected with no marked shrinkage.

The addition of talc to the batch speeds up the rate of shrinkage.

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(30) Vachuska, E.J., and G.A. Bole, 'Notes on kyanite and diaspore refractories'. J. Am. Ceram. Soc. 10, 761, (1927).

so as to bring total shrinkage nearly to completion in a very short time, and at a lower temperature.

Lesar, Krinbill, Jr., Keller and Bradley (31) have controlled the volume of fireclay and high alumina refractories on reheat by addition of sulphur compounds. They carried out experiment with various soluble compounds of sulfur and finally found that sulfuric acid can be most effectively and practically used. Microscopic examination of such bricks show that such expansion effected by sulfur compounds is caused by the formation of gas filled pores produced at high temperatures. The extent to which this gaseous expansion takes place as measured by increase in volume of the refractory body, is greater the higher the temperature to which the body is reheated.

The increased additions of the compounds of sulphur were found to effect increased expansion in most of the mixes examined. The reheat property thus can be adjusted for special service conditions by controlled addition of sulfur compounds. The manufacturing shrinkage may be adjusted by addition of grog and all reheat shrinkage be compensated by addition of an appropriate quantity of soluble sulphur compound. The modulus of rupture usually is increased by the addition of sulphur compounds.

Secondary Expansion of High Alumina Refractories

Several reactions which cause this secondary expansion have been noted previously. The conversion of quartz to tridymite and to cristoballite cause expansion because the latter minerals have lower density.

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(31) Lesar, R.A., Krinbill, C.A., Jr., Keller, W.D., and R.S.Bradley, 'Effects of compounds of sulphur on reheat volume change of fireclay and high alumina refractories. J. Am. Ceram. Soc. 29, 70, (1946).

Bricks with vesicular or bleb structures may also show expansion on reheat. Many non-plastic clays show a type of secondary expansion which is caused by opening of lamination in the clay during firing.

Hall (32) has investigated another type of reaction which produces secondary expansion in high alumina refractories. This is the only work reported in the literature which approximates the present problem but throws little light on this investigation. Hall used Missouri diaspore, Georgia bauxite, Missouri flint clay and Georgia kaolin for his investigation. He calcined each material in a different manner and made many batches consisting of these calcined materials plus the raw clay. He used one raw clay as a bond for the other calcined clay. Briquetts of 3 1/2 x 1 x 3/4'' were made using the dry press forming method, and were slowly fired to 2200° to 2900°F. Then he subjected briquetts to reheat test and recorded all change by measuring their lengths before and after the test.

All the diaspore grog bricks expanded on reheat. The secondary expansion in general increases linearly with the temperature. Bodies containing 72.1% kaolin grog and 27.9% raw diaspore exhibited a secondary shrinkage. As in the case of diaspore grog, all the bauxite grog briquetts expanded on refiring. It is shown by reheat curves that the secondary expansion varies with the mechanical properties of the grog which is produced by different methods of calcination. The preparation treatment of the grog has a considerable quantitative

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(32) Hall, J.L., Secondary expansion of high alumina refractories, J. Am. Ceram. Soc. 24, 348, (1941).

effect on secondary expansion of the body. By examination of thin sections of the bodies he shows that (1) in the bodies that exhibit secondary expansion, a ring of mullite development, which increases on refiring appears in the outer portion of the diaspore grain; (2) that in the bodies compounded of kaolin grog and diaspore clay, the increased mullite development is in the bond and these bodies show secondary expansion. Therefore, he concludes that secondary expansion of bodies having high alumina bonded with fireclay is caused by the increase in the size of the grog grains. This volume increase of the high alumina grog grains is brought about by silica transformed from the fire clay which reacts with corundum in the grog to form mullite. So, in fact the change in the volume i.e. expansion is the result of the transfer of silica from kaolin to diaspore. This transfer of silica could take place by diffusion through the glassy matrix or by volatilisation and transfer across the void spaces. In thin sections it is noted that if the former reaction occurs, the reaction edge would be expected to be thicker and crystals developed better in those portions of the grog grains immediately adjacent to the point at which the grog grain and matrix contacts. If vaporization takes place, the thickness of the reaction edge of each grog grain should be nearly uniform around the entire circumference which is not the case.

Therefore it is obvious that the transfer of silica takes place through the movements in the liquid phase, that is by diffusion. To summarize the work, permanent expansion in refired bodies that are compounded of high alumina grog bounded with fire clay is caused by the increase of volume of high alumina grog grain. The grog expands because of the influx of the silica from the fire clay through the liquid phase, the silica continuing with corundum of the grog to form mullite.

DISCUSSION OF RESEARCH

Raw Materials

Diaspore clay, Dutch Guiana bauxite and Weatherall plastic fire clay are the raw materials used in this investigation. High alumina grog is prepared by calcining bauxite and diaspore clay at various temperatures. The Weatherall plastic fire clay is used as the bond.

The diaspore clay used in this study is chiefly found in the sinkhole deposits of South Central Missouri. Though the occurrence is mainly in this area, a few exceptions are known in the northern districts. This diaspore clay is a spongy rough textured hard mass, light gray in color. Some stray red spots of iron may be found in big chunks of the clay, while some of the iron free variety is almost white. This diaspore clay is known as No. 1 diaspore clay.(33) Such a designation is given on the basis of the alumina content which grade carries more than 70% alumina. The lower grades are termed as No. 2 and No. 3 or sometimes known as Burley clay. No. 2 diaspore clay has an alumina content between 65 to 70% and clays having alumina content from 60 to 65% are designated as No. 3 clay or Burley clay.

Mineralogically the diaspore clay seems to be composed of two fractions, a hydrated oxide and a complex aluminum titanium silicate. These facts are evident from the chemical analysis given on page 30. The analysis shows high alumina content as well as titania and combined water. Though no effort was made to determine the type of

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(33) H.S.McQueen, Geology of the fire clay districts of East Central Missouri, Mo. Geological Survey and Water Resources, Vol. XXVII, second series, pp. 157 (1943)

aluminum hydrate present, it was assumed to be diasporite as has been reported in the literature (33). The Pyrometric Cone Equivalent of No. 1 diaspore clay is around Cone 36-37.

The Dutch Guiana bauxite used is of high purity and quality, having an alumina content about 60%. The silica is comparatively much lower, but the combined water is high being about 30%. This high alumina content and high combined water suggests that the bauxite is nothing else but the mineral gibbsite with some impurities. The main impurities are SiO_2, TiO_2, and Fe_2O_3. The bauxite is fine grained, rough textured, and light pink in color. The grain size averages from fine to coarse. The detailed mineral composition and properties of this bauxite are discussed in the review of literature. The chemical analysis is given on page 30 .

The Weatherall plastic fire clay is one of the member clays of the Chelthenham formation and gets the name from the Weatherall pit where it is mined. The lithological character of this plastic fire clay are described by McQueen (34) as:-

''The clay of the upper member is uniform in general make up. It is nearly always bluish gray in color. It is fine grained, but lacks the smooth even texture of lower clays. It is not as hard, and slickensided surfaces of the lower clays are almost lacking and when present are not as highly developed. The clay has similar mode of fracture, that is with conchoidal surfaces and fairly sharp edges,

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(34) H. S. McQueen, Op. cit.

but in neither is the development as pronounced as in the lower clays''.

''Two features, however, serve to distinguish the clay. First, the clay upon weathering slacks or breaks down into extremely fine angular particles and second with prolonged surface weathering it becomes a gray, sticky highly plastic mass''.

The above description generally fits the clays of the formation mentioned, and the plastic fire clay used in the investigation being a member, can be easily adapted.

This plastic fireclay is hard, smooth textured, fairly plastic and dark gray in color. The chemical analysis of this clay shows that its mineral composition is much closer to the mineral kaolinite. Mueller (35) who used the same clay for his investigation, has examined it petrographically and showed that kaolinite is the chief mineral constituent of the plastic clay. It has other minerals such as pyrite, calcite and quartz crystals as impurities.

The chemical analyses of all the raw materials used are given in Table III on page 30 .

Calcination of Clays and Preparation of High Alumina Grog

The diaspore clay and bauxite as received were in the form of large chunks. There were first reduced in size by breaking them with a hammer. The broken pieces were then further reduced in size by

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(35) J.I.Mueller, 'A Study of gelation of air-setting refractory mortars', Ph.D. Thesis, University of Missouri, Page 21, (1949).

crushing them through a jaw crusher. The crushed material from the jaw crusher was further reduced in size through a roll crusher so as to give a grain size of around 3 mesh. This crushed material was then passed through a 3 mesh sieve, so as to get evenly sized material for calcination. Thirty pounds of diaspore clay and bauxite was thus prepared for calcination.

The high alumina grog is to be prepared by calcining the crushed materials at 1400°, 1500° and 1600°C. For calcination, no briquettes or balls were prepared, but the crushed material as such was calcined. This developed a problem of providing a suitable container which would stand the calcination temperature and not react with the material to be calcined. Refractory crucibles supplied by Denver fire clay were quite satisfactory up to 1400°C, and therefore they were used for calcination of bauxite and diaspore at 1400°C. For calcination at temperatures higher than 1400°C a special container was prepared using pure alumina by the casting process. Pure alumina was finely ground in a ball mill and a casting slip (36) was prepared. Using this slip, rectangular containers 10'' x 4'' x 4'' in size were cast in a previously prepared plaster of Paris mould. The cast containers had very little mechanical strength so they were initially fired at 1200°C. These containers could be used at the higher calcination temperatures, without any difficulty.

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(36) Planje, T.J.M., 'A study of ionic mobility of alkali ions in dilute alkali borox trioxide glasses as deduced from space change considerations'. Ph.D. Thesis, University of Missouri, Appendix A., July, 1950.

TABLE III

Chemical Analysis of Raw Materials

SiO_2	10.45	4.60	47.76
Al_2O_3	70.11	60.76	36.39
Fe_2O_3	1.75	1.51	1.23
CaO	-	-	0.22
MgO	0.15	-	0.34
TiO_2	2.80	2.32	1.68
Alkalies	0.70	0.20	0.50
Ignition Loss	13.89	30.5	11.76
	99.85	99.89	99.88

A - Missouri diaspore clay
B - Dutch Guiana bauxite
C - Missouri Weatherall plastic fire clay

A fixed firing schedule was observed for all calcination firings. The calcination temperature was reached within five hours and was held for two hours. Both the bauxite and diaspore clay were calcined in the same furnace at the same time at the specified temperatures so that each material received an even and similar calcination treatment. Throughout calcination an oxidizing atmosphere was maintained. The furnace was electrically fired.

The calcined material was then further crushed so as to get 8 mesh grog for preparation of the raw batch. The crushing was carried out in the roll crusher and all the resulting grog was passed through a U.S. Standard sieve No. 8. The coarser sizes were repeatedly crushed till all passed through 8 mesh. In this operation, special care was taken not to crush the material much finer, but to maintain an even sized crushed material.

The Weatherall plastic fire clay is used in the raw condition as a bond. The batch requires that the plastic fire clay be crushed through a 20 mesh sieve. The same procedure for crushing was adapted as described above excepting that for the final crushing a hammer mill was used in place of the roll crusher. The hammer mill produces fairly evenly sized crushed material which is just about 20 mesh in size. All the crushed material was then passed through a U.S. Standard sieve No. 20.

During the calcination process all the volatile and chemically combined materials which cause much of the shrinkage are removed. If insufficient calcination is done, some of these volatile constituents are not removed. Such grog if used in service would cause further shrinkage. It is therefore necessary to know to what extent the calcination has been effected. To determine the extent of calcination, the calcined material was first finely ground and then ignited at high temperatures in a platinum crucible. The resulting loss on ignition indicated the degree of calcination. The results obtained on the high alumina grogs are given in the following table.

TABLE IV

Loss on Ignition of Calcined Clays

	A	B	C	D	E	F
Loss on Ignition	0.06%	0.03%	0.04%	0.06%	0.08%	0.05%

A - Bauxite calcined at 1400°C
B - Bauxite calcined at 1500°C
C - Bauxite calcined at 1600°C
D - Diaspore calcined at 1400°C
E - Diaspore calcined at 1500°C
F - Diaspore calcined at 1600°C

Loss on ignition was actually determined accurately to the fourth decimal place, but for tabulation it was corrected to the second place.

A sieve analysis of all the high alumina grog and bond clay was run as per A.S.T.M. (37) C-92-46. The sieve analysis gives an idea of the particle size distribution of the batch to be used in making

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(37) Op. cit. page 95.

brick. As all the materials were crushed through 8 mesh, the coarsest sieve used was 8 mesh and the finest one was 200 mesh. The intermediate sieves used are 20, 40, 60, 80 and 100 mesh.

A weighed amount of each grog was placed on the top sieve. The sieves were arranged in order of the size with coarsest sieve at the top and the finest at the bottom. A receiving pan was also placed at the bottom. After the sample is poured on the top sieve the remainder is placed in a mechanical sieving machine and run for 15 minutes. The percentage of material retained on each sieve and through 200 mesh was then calculated on the basis of the original weight. The result of complete sieve analysis is shown in Table V.

Batch Calculations

The batch calls for:- 70% Al_2O_3 in the refractory bricks.

From the chemical analysis of the raw materials it is noted that -

Al_2O_3 content of the raw diaspore - 70.11%

and loss on ignition is - 13.89%

$\therefore$ on calcination the diaspore clay will have:-

$$\frac{70.11 \times 100}{86.11} = 81.5\% \ Al_2O_3 \text{ content.}$$

Al_2O_3 in raw bauxite - 60.76%

Loss on ignition - 30.5

Then calcined bauxite will have:-

$$\frac{60.76 \times 100}{69.5} = 87.5\% \ Al_2O_3 \text{ content.}$$

The Weatherall plastic clay is used as raw clay and has an Al_2O_3 content of 36.39%.

If x is the amount of calcined clay (grog) in the 70% Al_2O_3 refractory brick, the remaining bond clay - plastic fire clay would be (100-x). As Al_2O_3 is derived from both these constituents, to make 70%, the following equation can be formed for the bauxite batch.

$$\frac{87.7x}{100} + \frac{36.39\ (100-x)}{100} = 70$$

By solving the equation the batch is calculated as

65.9% calcined bauxite (grog)

34.1% raw plastic fire clay

Similarly the batch for diaspore clay can also be calculated:

$$\frac{81.5x}{100} + \frac{36.39(100-x)}{100} = 70$$

Solving the equation, the batch is

74.6% calcined diaspore (grog)

25.4% raw plastic fire clay.

All the bodies using various temperature calcined bauxites and diaspore were prepared according to these calculated batches.

Forming and Firing of High Alumina Refractory Bricks

The grog and the bond clay were weighed and placed in a small Simpson mixer. First, the batch was mechanically mixed perfectly in the mixer in the dry condition and then water was slowly added while the mixer was running. The batch required 10% water for safe working to dry press the bricks. This was determined by trial and error. After addition of small amounts of water the batch was formed in the dry press and tested for strength. This process was repeated until strong dry press brick were obtained. The batch is mixed with water till a good homogenious mixture is obtained.

TABLE V

Sieve Analysis of High Alumina Grogs and Raw Plastic Fire Clay

	A	B	C	D	E	F	G
On 8 mesh	0.70	0.40	0.10	1.00	0.20	0.80	-
On 20 mesh	25.37	26.78	36.0	46.75	32.08	35.17	0.45
On 40 mesh	25.00	25.71	28.18	20.35	22.77	23.02	38.70
On 60 mesh	13.76	13.37	13.13	9.24	12.60	10.28	19.68
On 80 mesh	5.90	5.57	5.08	3.76	5.52	4.40	9.00
On 100 mesh	4.25	4.05	3.29	2.80	4.20	3.43	5.77
On 200 mesh	13.90	12.50	8.67	7.95	12.00	10.16	20.00
Through 200 mesh	11.12	11.62	5.55	8.15	10.63	12.74	6.40
	100.0	100.0	100.0	100.0	100.0	100.0	100.0

A - Grog prepared by calcining bauxite at 1400°C
B - Grog prepared by calcining bauxite at 1500°C
C - Grog prepared by calcining bauxite at 1600°C
D - Grog prepared by calcining diaspore clay at 1400°C
E - Grog prepared by calcining diaspore clay at 1500°C
F - Grog prepared by calcining diaspore clay at 1600°C
G - Weatherall plastic fire clay (-20 mesh).

A Hydr-oil press was used to press the bricks. The pressure used was 1800 psi which is commonly used in the industry for making refractory bricks. The mold size is 6 1/2'' x 1'' x 4''. To get evenly sized bricks after the pressing, a weighed amount of batch was pressed each time. This gave blocks of exact size and weight within an error of 1% in height in the direction of applied pressure. About 20 bricks were made and then dried in air for about two days and further at 110°C for 24 hours.

The firing of these bricks was carried out in a globar fired electric furnace all at the same time. The bricks were set in such a way that all bricks received an even heat treatment from all sides. All bricks were fired to cone 14 in 8 hours and were held at that temperature until cone 15 soaked down. This firing schedule was chosen so as to give a heat treatment to the bricks similar to that given in industry for high alumina refractories.

The furnace was allowed to slowly cool, after which all pieces were removed from the furnace. Each brick was then measured for total firing shrinkage. The results are shown in the following table.

TABLE VI

Total Initial Firing Shrinkage on Refractory Bricks

	A	B	C	D	E	F
1	0.93%	0.93%	0.93%	-	-	-
2	0.93	0.93	0.93	-	-	-
3	0.93	1.2	0.93	-	0.5	-
4	0.93	0.96	0.93	-	0.5	-
5	1.2	0.93	0.96	0.5	0.5	-
6	0.94	0.93	0.93	-	-	0.5
7	0.96	0.94	0.94	-	-	0.5
8	1.2	0.93	0.93	0.5	-	-
9	0.93	0.93	0.93	-	-	-
10	0.93	0.93	1.2	-	0.5	-
Average	0.98	0.98	0.96	0.1	0.2	0.1

A - Bauxite brick - bauxite calcined at 1400°C
B - Bauxite brick - bauxite calcined at 1500°C
C - Bauxite brick - bauxite calcined at 1600°C
D - Diaspore brick - diaspore calcined at 1400°C
E - Diaspore brick - diaspore calcined at 1500°C
F - Diaspore brick - diaspore calcined at 1600°C

Reheat Change

The standardized test for reheat change is carried out as per A.S.T.M. test (38) C-113-46 for reheat change of refractory bricks. The procedure outlined was strictly followed except for the measuring methods.

The A.S.T.M. procedure is strictly designed for 9'' straight bricks and therefore recommends that the dimensions shall be measured to the nearest 0.02''. For such measurement a firm joint caliper would serve the purpose, but would be unable to record minor changes which would occur for smaller bricks such as handled in the present investigation. Therefore, it was felt that a precision measuring device reading accurately to 0.001'' should be used to record such minor changes. Such an instrument was built in the laboratory and is shown in illustration No. 1 on page 39.

The instrument consists of a dilatometer attached to a handle which can be freely raised or lowered by turning a knob. The dilatometer dial is divided into 100 divisions and each division is equivalent to 0.001''. As the dilatometer goes up or down a synchronised index also moves up or down along the scale attached on the left side of the column. Each division of the scale reads 1/64 of an inch. A magnifying lens is permanently fixed in front of the index so that it also moves up or down with index. By the use of this lens the index can be accurately read. The sample to be measured rests on

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(38) A.S.T.M., Op. cit., p. 80.

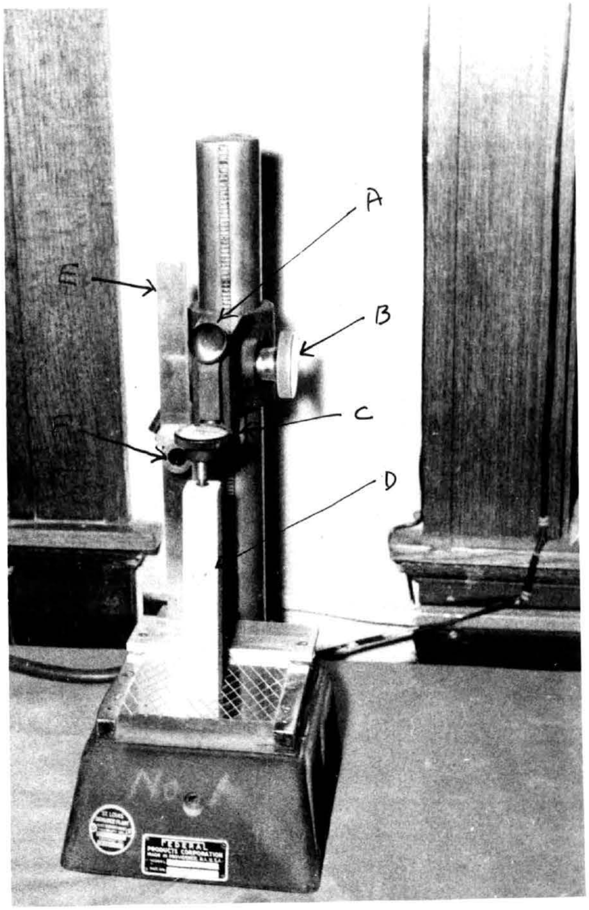

Fig. 1: The precision measuring device used for this investigation to measure reheat changes of refractory bricks. Lengths accurate upto 0.001'' can be easily measured.

A - Finer adjustment knob, B - Turning knob to raise or lower the micrometer dial and index, C - Micrometer dial, D - High alumina refractory brick, E - Scale with 1/64'' divisions, F - Magnifying lens. Index is behind the lens.

the smooth steel surface platform. To measure the dimension, the dilatometer is slowly lowered and the button of the dilatometer is brought close to the surface of the sample. If at this time the index is somewhere between two divisions on the scale, the dilatometer is further lowered till the index is set on the lower division line. In this position the dilatometer is under pressure and therefore would record any length which is above the division where the index is set. Readings are taken on the scale to 1/64 of an inch. After converting the scale reading into decimals, the dilatometer readings are added to it. Thus, a very accurate change to 0.001'' can be recorded with ease. The main features of this instrument is the ease of recording and accuracy.

Three bricks from each lot were picked for the test, and lengths were accurately measured by the above described device. Each of these bricks was placed on dummy brick selected from the same lot, on their 6 1/2'' x 1'' face. A granular alumina layer was placed on the top of the dummy, and over it the test brick was placed.

The globar electric furnace was used for firing the test pieces. This furnace having small interior area, could be heated up fast and would distribute heat evenly through the entire area. The test bricks placed on dummy brick are loaded in the furnace so that they are about 1'' apart from each other.

The reheat change test was run at two different temperature schedules, schedule B and C of A.S.T.M. C-113-46 test for reheat change. The schedules are as follows:-

TABLE VII

	Schedule B	Schedule C
1 hour	Between 900° and 1000°C	Between 900 and 1000°C
2 hours	Between 1275 and 1325°C	Between 1275 and 1325°C
3 hours	Reach 1400°C and then maintain for 5 hours	Between 1450 and 1500°C
4 hours		Between 1550 and 1575°C
5 hours		Reach 1600°C then maintain for 5 hours

The temperature for schedule B was measured with a platinum + 10% rhodium thermocouple and were controlled by a Micromax. For schedule C, at temperatures higher than 1400°C, the temperatures were read by a radiation pyrometer and controlled by the Micromax. The temperature schedules were strictly followed by the use of a program control working in conjunction with the Micromax.

The furnace was allowed to cool slowly, and when the test bricks reached room temperature, their lengths were measured again. Measurements were made on three bricks of each batch, and the percentage change was calculated on the basis of the original length. An average of the three bricks is reported in the following table.

TABLE VIII

Reheat Change of Bauxite and Diaspore Bricks

	A	B	C	D	E	F
Reheat change as per A.S.T.M. C113-46 Schedule B(1400°C)	-0.46*	1.21	0.056	0.54	1.09	0.84
Reheat change as per A.S.T.M. C113-46 Schedule C(1600°C)	0.052	3.66	1.506	1.22	0.67	-0.95

* - indicates shrinkage

A - Bauxite brick made using bauxite calcined at 1400°C
B - Bauxite brick made using bauxite calcined at 1500°C
C - Bauxite brick made using bauxite calcined at 1600°C
D - Diaspore brick made using diaspore calcined at 1400°C
E - Diaspore brick made using diaspore calcined at 1500°C
F - Diaspore brick made using diaspore calcined at 1600°C

From Table VIII it is seen that A shrinks on reheat at 1400°C, but on reheat at 1600°C shows a very small expansion. B, the bauxite brick containing bauxite calcined at 1500°C, shows a considerable expansion at 1400°C and more than twice as much as at 1600°C. The brick C does not show any appreciable change at 1400°C, but at 1600°C has an expansion of about 1.5%. Diaspore bricks show a change such that no similarity can be drawn with the bauxite bricks. Brick D expands a small amount at 1400°C and on reheat at 1600°C expands further. Brick E initially shows expansion at 1400°C, but starts shrinkage at the higher heat treatment of the reheat test. This process is quite distinct in brick F. After expanding about 0.8% at

1400°C, it starts shrinking on reheat at 1600°C and shows appreciable shrinkage.

The effect of reheat temperature has been noted above, but now will be considered the change taking place in the bricks after reheat at the same temperature but having grog prepared by various calcination temperatures. The bauxite brick (brick A) having a grog calcined at 1400°C shows shrinkage. Brick B, using grog of 1500°C expands, and as the calcination temperature is further increased as in brick C, it shows less expansion, i.e., it has shrunk.

Diaspore bricks after reheat at 1600°C behave in the same way as bauxite bricks. Lower calcined material shows little expansion, which increases as calcination temperature is increased, but on further increasing the temperature, a small shrinkage is effected. Bauxite bricks reheated at 1600°C show the same behavior as the same bricks reheated at 1400°C. It is not true with diaspore bricks. For diaspore bricks, there is a large expansion for bricks of lower calcined grog, and they shrink a littl bit as calcination temperature is increased, and with 1600°C calcined material, considerable shrinkage is effected. Thus it is evident that the calcination temperature of the raw material has a direct effect on the behavior of bricks in the reheat test. Changes such as mineralization, crystal growth, and fusion takes place during calcination. These changes control the expansion or shrinkage.

In the following pages, are reported the various methods of investigation used for determining the cause of the behavior of the bricks on reheat. By x-ray diffraction and petrologic examination, mineralization as well as crystal growth is determined. Physical properties such as porosity and linear thermal expansion are also determined.

Porosity

The porosity of refractories is the ratio of the volume of pores or voids in a body to the total volume of the body. This ratio is usually expressed as a percentage. The porosity of the fired sample is due to both closed and open pores, while the apparent porosity includes only those pores which are open and can be easily filled in by air or water.

Changes in porosity have direct relation to the expansion or shrinkage behavior of fire clay refractories. On firing the bricks, when the porosity is increased due to heat treatment, the brick eventually shows an expansion of permanent nature. When the brick contains volatile materials which at high temperature give out gases, it would also show an expansion on firing due to evolution of gas and expansion of the gas trapped in the pores. Sometimes such expansions are disastrous and the brick may bloat or form a bleb structure and ruin the ware. Conversely when bricks are fired to a higher temperature, that is overfired, the glassy phase is formed which occupies the pore space of the bricks and results in total shrinkage of the bricks. This shrinkage depends upon the amount of glass formed, and the decrease in porosity. As more and more glassy phase is formed on firing, a stage is reached when bloating or vesicular structure is developed, giving an overall increase in volume and expansion. Such a structure gives an increase in porosity also. Therefore, overfiring may be indicated by either decrease or increase in porosity. The changes in porosity also indicate a measure of refractoriness. A decrease in porosity and volume indicates the progress toward vitrification and when these changes are plotted in the form of curves, the slope of the curve indicates the rate of vitrification.

Apparent porosity can be determined chiefly by two methods. The first one is by the gas expansion method (39). The sample is placed in an airtight container which is then evacuated. After evacuation the pressure in heighth of a column of mercury is read. Then the evacuated container with sample is connected with another closed container whose volume is previously known. On connecting, the air from the second container, rushes to the evacuated container and a drop in pressure takes place. This drop in pressure is directly related to the volume of air entering the evacuated container and the volume can be determined by the gas law. If the bulk volume of the brick and the total volume of the first container is known, the volume of the pores in the brick can be calculated and the porosity be determined.

The second method as outlined by A.S.T.M. is designated C-20-46(40) for refractories.

The cause of expansion or shrinkage of bricks on reheat may be due to the change in porosity as discussed above. Therefore to determine the cause of reheat changes on the test bricks, apparent porosity of the fired bricks and reheated bricks was determined. As the test pieces are small in size the gas expansion method is not

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(39) H.T.S. Swallow, Apparatus for determination of the porosity of fire bricks by gas expansion. Trans. Eng. Ceram. Soc. 36, 384 (1936)

(40) A.S.T.M., op. cit., 89.

practicable. Also it is not widely used in industry. Therefore the A.S.T.M. procedure was adopted.

All the bricks were initially dried to a constant weight at 110°C to remove absorbed moisture. After determining the accurate weight, all bricks were immersed in boiling water for four hours. During the boiling period they were entirely covered with water and care was taken that they were not in contact with the heated bottom of the container. After boiling, the specimens were cooled slowly to room temperature, while still covered by water. The saturated weight and suspended weight in water of these bricks was then determined.

If D is the dry weight of the specimen, S, the suspended weight and W, the saturated weight, the percentage apparent porosity P is

$$\%P = \frac{W-D}{W-S} \times 100$$

The results are shown in Table IX.

TABLE IX

Apparent Porosity of Bricks Before and After Reheat at 1400°C and 1600°C

A - Bauxite Brick - Bauxite calcined at 1400°C ----- 38.0%

B - Bauxite Brick - Bauxite calcined at 1500°C ----- 32.5%

C - Bauxite Brick - Bauxite calcined at 1600°C ----- 36.1%

D - Diaspore Brick - Diaspore calcined at 1400°C --- 39.0%

E - Diaspore Brick - Diaspore calcined at 1500°C --- 38.0%

F - Diaspore Brick - Diaspore calcined at 1600°C --- 38.8%

G - Brick A, reheat at 1400°C --------------------- 35.4%

H - Brick B, reheat at 1400°C --------------------- 34.0%

I - Brick C, reheat at 1400°C --------------------- 35.8%

J - Brick D, reheat at 1400°C --------------------- 39.2%

K - Brick E, reheat at 1400°C --------------------- 39.9%

L - Brick F, reheat at 1400°C --------------------- 40.6%

M - Brick A, reheat at 1600°C --------------------- 35.2%

N - Brick B, reheat at 1600°C --------------------- 38.2%

O - Brick C, reheat at 1600°C --------------------- 37.6%

P - Brick D, reheat at 1600°C --------------------- 37.2%

Q - Brick E, reheat at 1600°C ------ -------------- 38.4%

R - Brick F, reheat at 1600°C --------------------- 36.7%

Shrinkage and Expansion Behavior of Bricks

For an exact study of reheat changes taking place in a brick during reheat firing, it would be necessary to know exactly at what temperature such changes are starting to take place when they are complete. Such a study would necessitate measuring expansion or shrinkage while the brick is actually being heated.

Methods of measuring expansion continuously have been discussed in the review of literature. The method adopted for this investigation is an indirect one. The expansion of the brick is transferred to a rod which moves, and the movement of this rod is measured outside the furnace by a measuring telescope. All measurements previously recorded in the literature, for refractory bricks were most commonly made up to 1000°C. The present investigation requires temperatures much higher than that. For this purpose a special furnace was constructed which is shown in figure 2.

This is a globar fire muffle furnace. The interior dimensions of the furnace are just big enough so as to easily accomodate a 9'' straight brick. Outside the muffle a brick work of insulating fire bricks is made while the outermost frame of the furnace is made from transite sheets, and the space between the insulating brick work and outer frame is further insulated with magnesia. The furnace has a loading device from the bottom which is controlled by air pressure. When the air is turned into the bottom of the cylinder, the piston which supports the brick is raised up till it exactly fits the bottom hole of the muffle. If the air is turned into the top of the cylinder the piston is forced down and the specimen is removed from the furnace.

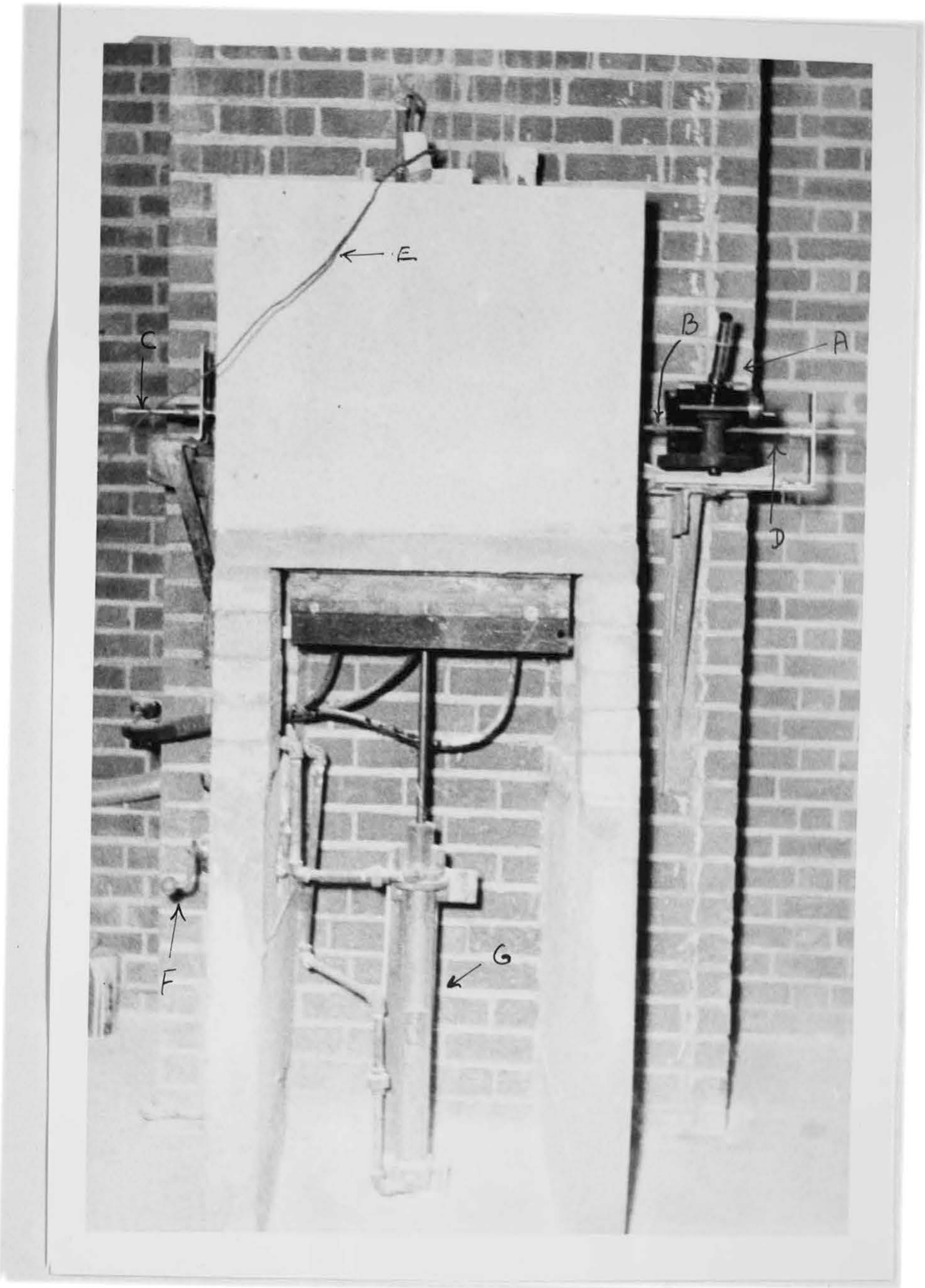


Fig. 2: **Furnace** used for measuring expansion or shrinkage of **refractory** bricks. A - Travelling telescope, B - Silicon carbide **rod,** C - **Fixed** end of the left side silicon carbide rod, D - Metallic tube with spring, E - Thermocouple lead wires, F - Two way air valve, G - Air cylinder with piston supporting brick to be loaded. The furnace as seen in the picture is already loaded.

Thus the brick whose expansion is to be measured is placed in the muffle. From the side holes of the furnace two silicon carbide rods are inserted against two sides of the bricks. The rod on the left hand side is permanently fixed in a metal tube, while on the right another rod is attached to the tube having a metallic spring. This spring keeps the silicon carbide rod constantly pressed against the brick which in turn is pressed against the fixed rod on the other side. This spring is easily compressible so that a slight change in the dimension of the brick will easily deform it so as to keep a constant pressure on the rod. Thus when the bricks is heated, and if expansion occurs, the silicon carbide rod would be pushed out. In event of shrinkage, the rod would of course beforced in. This movement of the rod would thus exactly indicate the extent to which expansion or shrinkage has taken place at a specific temperature. On the rod which is in contact with the spring, a permanent index work is made. As the rod is pushed out or in, the index would also move. The movement of this index is then measured by a travelling telescope which moves on a vernier scale giving accurate readings upto 0.001 cm. The special feature of this furnace is that it can be heated at much higher temperatures, and measurement of expansion or shrinkage can be easily made at temperatures to 1600°C although it was not necessary to exceed 1500°C for this experiment. Silicon carbide rods were used as they would stand the elevated temperature without deformation.

At higher temperature silicon carbide rods also expand, and the expansion noted would be combined effect of the rod as well as brick.

For this purpose, the expansion of the rods was standardized for the high temperatures at which the experiment is performed. The standardization was carried out with a silica glass slab exactly equal in dimension to the brick. As the silica glass has a very small coefficient of expansion, the expansion indicated would be only due to silicon carbide rods. Thus measurements were made up to 1000°C and were plotted against the temperatures. The curve showed practically a linear relation between expansion and temperature up to 1000°C. Assuming that this relationship would hold good at further higher temperatures also, the curve was extended further so as to give expansion up to 1600°C. Thus from the readings taken for the expansion of brick at a particular temperature, the expansion for the rods is subtracted, and the net expansion after deduction would be due to the brick alone. All expansions are plotted as percentage based on the original length of the specimen. All the temperatures were measured using a platinum-10% rhodium thermocouple.

Such measurements were made on bauxite and diaspore bricks where the calcined material at various temperatures is used. Results are shown in Table X and are plotted on graphs 1 and 2.

TABLE X

Data on Expansion of Bauxite Brick

Bauxite calcined at:

1400°C		1500°C		1600°C	
T°C.	% Exp.	T°C.	% Exp.	T°C.	% Exp.
210	0.029	234	0.095	310	0.004
354	0.048	344	0.097	390	0.03
436	0.075	386	0.104	428	0.08
514	0.093	442	0.131	470	0.08
580	0.162	484	0.145	560	0.096
636	0.170	524	0.155	642	0.13
686	0.187	570	0.160	696	0.15
736	0.210	642	0.220	816	0.185
788	0.230	666	0.240	854	0.20
826	0.265	696	0.250	904	0.24
890	0.36	728	0.28	972	0.28
1004	0.39	762	0.28	1024	0.25
1038	0.43	788	0.36	1074	0.41
1076	0.46	825	0.41	1136	0.44
1126	0.475	880	0.37	1160	0.57
1156	0.535	916	0.40	1180	0.57
1177	0.60	978	0.41	1240	0.53
1206	0.62	1006	0.46	1264	0.56
1225	0.585	1046	0.49	1328	0.545
1312	0.60	1086	0.47	1362	0.51
1346	0.58	1114	0.50	1384	0.51
1366	0.555	1144	0.49	1420	0.47

TABLE X (cont'd)

1400°C		1500°C		1600°C	
T°C	% Exp.	T°C.	% Exp.	T°C.	% Exp.
1392	0.515	1170	0.50	1450	0.37
1416	0.44	1190	0.51	1486	0.24
1426	0.40	1208	0.51	1498	0.11
1442	0.275	1290	0.50		
1468	-0.06*	1342	0.51		
1488	-0.38	1392	0.47		
1510	-0.75	1408	0.47		
		1434	0.44		
		1458	0.43		

* - indicates shrinkage

TABLE XI

Data on Expansion of Diaspore Bricks

Diaspore calcined at:

1400°C		1500°C		1600°C	
T°C	% Exp.	T°C	% Exp.	T°C	% Exp.
260	0.119	310	-0.04*	348	-0.063*
374	0.119	370	-0.034	416	-0.048
414	0.192	396	0.0	458	-0.024
450	0.20	432	0.01	500	-0.020
588	0.278	468	0.02	530	-0.004
652	0.325	502	0.025	550	0.0
697	0.385	544	0.04	620	0.027
716	0.44	586	0.07	690	0.04
742	0.41	608	0.05	742	0.09
800	0.39	632	0.06	770	0.135
850	0.43	686	0.06	830	0.140
888	0.43	724	0.11	872	0.180
910	0.45	788	0.15	918	0.210
942	0.69	843	0.16	960	0.240
968	0.51	900	0.20	1000	0.270
1006	0.55	938	0.20	1025	0.30
1078	0.57	980	0.20	1062	0.32
1100	0.605	1012	0.295	1084	0.35
1132	0.60	1042	0.34	1156	0.36
1158	0.61	1063	0.43	1200	0.41
1182	0.64	1089	0.47	1250	0.43

TABLE XI (cont'd)

1400°C		1500°C		1600°C	
T°C	% Exp.	T°C.	% Exp.	T°C	% Exp.
1202	0.64	1190	0.50	1282	0.45
1250	0.64	1252	0.61	1316	0.52
1274	0.65	1304	0.61	1362	0.52
1303	0.72	1349	0.60	1400	0.62
1356	0.65	1408	0.67	1432	0.63
1378	0.65	1434	0.72		
1408	0.60	1454	0.72		

* - indicates shrinkage

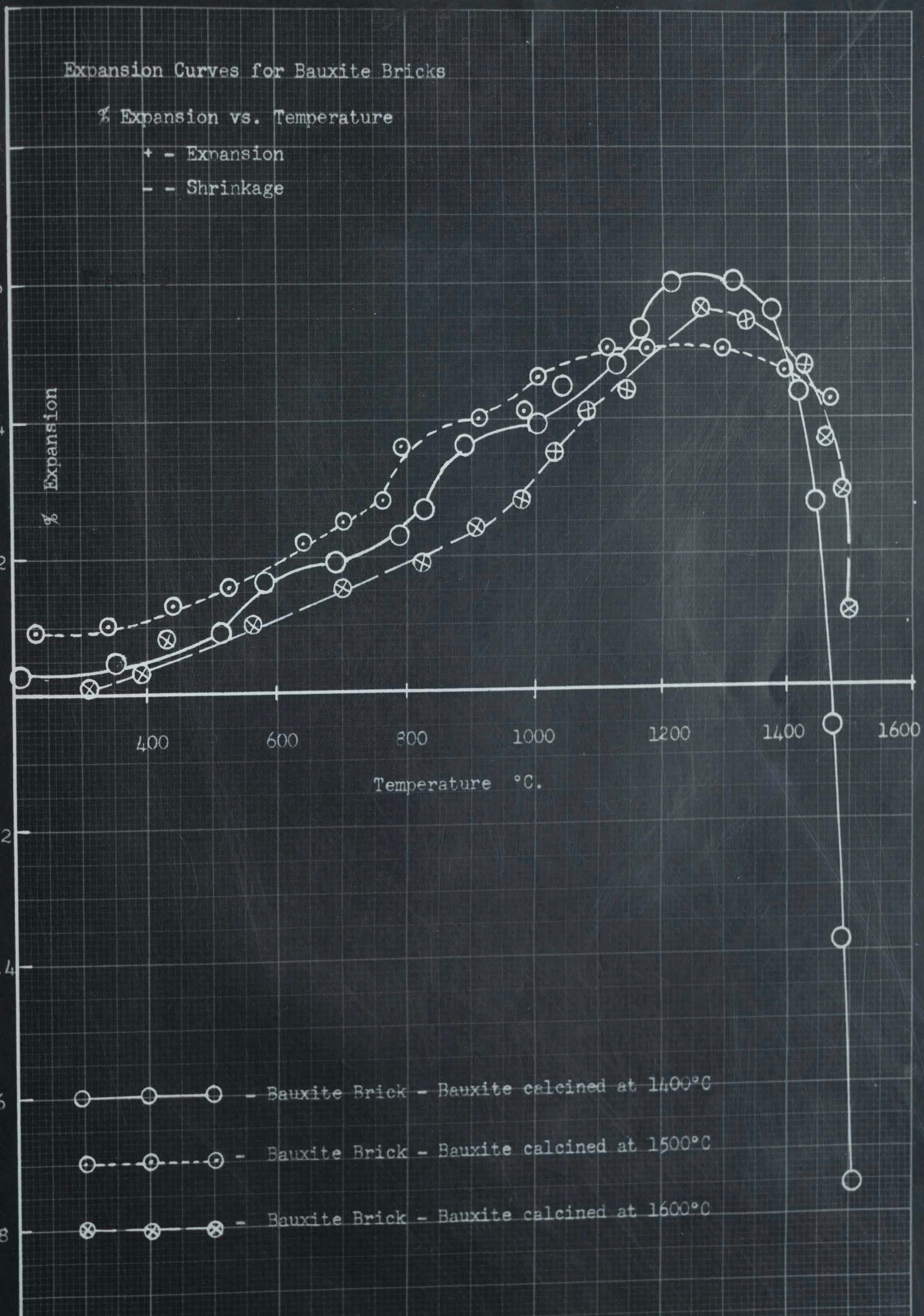
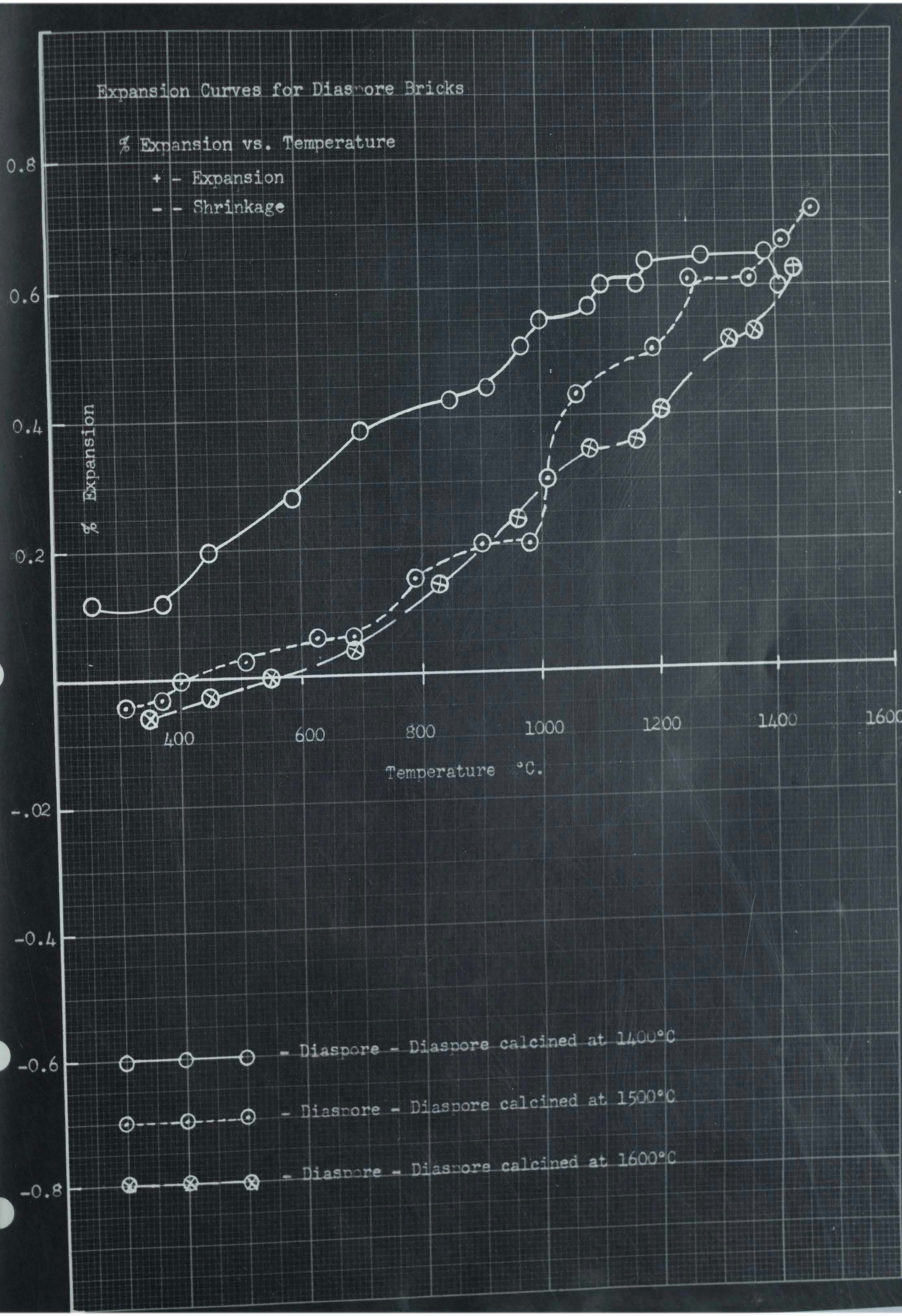


Figure 3

Expansion Curves for Bauxite Bricks
% Expansion vs. Temperature
+ - Expansion
- - Shrinkage
% Expansion
0.8
0.6
0.4
0.2
-0.2
-0.4
-0.6
-0.8
400
600
800
1000
1200
1400
1600
Temperature °C.
- Bauxite Brick - Bauxite calcined at 1400°C
- Bauxite Brick - Bauxite calcined at 1500°C
- Bauxite Brick - Bauxite calcined at 1600°C


Expansion Curves for Diaspore Bricks
% Expansion vs. Temperature
+ - Expansion
- - Shrinkage
% Expansion
0.8
0.6
0.4
0.2
-.02
-0.4
-0.6
-0.8
400
600
800
1000
1200
1400
1600
Temperature °C.
- Diaspore - Diaspore calcined at 1400°C
- Diaspore - Diaspore calcined at 1500°C
- Diaspore - Diaspore calcined at 1600°C

It would also be interesting to know the shrinkage or expansion behavior of the raw materials i.e. bauxite and diaspore clay. This would indicate the temperatures at which complete shrinkage would be effected. It is important to know this as the calcination treatment is one of the chief factors which governs the expansion or shrinkage of any brick made out of calcined material. When calcination is incomplete such a brick would shrink further when fired at temperatures higher than the calcination temperature. If calcination is completely removed, then any change on firing would be due to other than improper calcination.

To determine progressive shrinkage of the raw bauxite and diaspore, two bricks of 6 1/2'' x 1'' x 1'' in size were prepared by dry pressing the -20 mesh raw materials using only water as a bond. The pressure was the same as used for making the bricks. These bricks were dried to constant weight at 110°C and then were placed in the shrinkage furnace described in the preceding section and the measurements of the shrinkage were made up to 1500°C. The results are shown in Table XII and are plotted on graph 3.

In figure 5 are shown comparative sizes of the bars of raw bauxite and diaspore clay before and after firing. The bauxite bar has shrunk about 16% in length from the fired size. Comparatively, diaspore clay has very little linear shrinkage being about 3%.

TABLE XII

Shrinkage of Raw Bauxite and Raw Diaspore Clay

Bauxite		Diaspore Clay	
T °C.	% Shrinkage	T °C	% Shrinkage
254	-0.181*	292	-0.036
354	-0.357	396	-0.163
435	-0.290	478	-0.332
546	-0.006	560	-0.356
616	+0.139	628	-0.308
690	0.593	686	-0.259
752	0.756	738	-0.302
802	0.738	782	-0.302
850	0.835	826	-0.326
908	0.968	872	-0.326
956	1.107	910	-0.266
994	1.337	942	-0.163
1034	1.501	978	-0.0181
1064	1.743	992	+0.0181
1102	2.130	1012	0.0604
1130	2.554	1040	0.121
1158	3.159	1068	0.133
1182	3.761	1096	0.187
1208	4.406	1124	0.235
1230	5.042	1142	0.300
1250	5.690	1166	0.411

TABLE XII (cont'd)

Bauxite		Diaspore	
T °C	% Shrinkage	T °C	% Shrinkage
1270	6.295	1186	0.452
1288	6.961	1204	0.610
1308	7.282	1216	0.857
1324	7.784	1242	1.147
1338	8.129	1258	1.358
1356	9.061	1276	1.569
1366	9.915	1292	1.727
1382	10.69	1304	1.902
1392	11.54	1374	2.095
1410	12.86	1424	2.536
1426	14.09	1434	2.699
1442	14.72	1450	2.983
1450	14.98	1476	3.411
1458	15.20	1500	3.924
1466	15.45		
1476	15.67		
1494	15.88		

* - indicates shrinkage

Fig. 5: Shrinkage of raw bauxite and diaspore clay bar after firing up to 1500°C.

A - Raw diaspore bar

B - Raw diaspore bar after firing at 1500°C

C - Raw bauxite bar

D - Raw bauxite bar after firing at 1500°C.

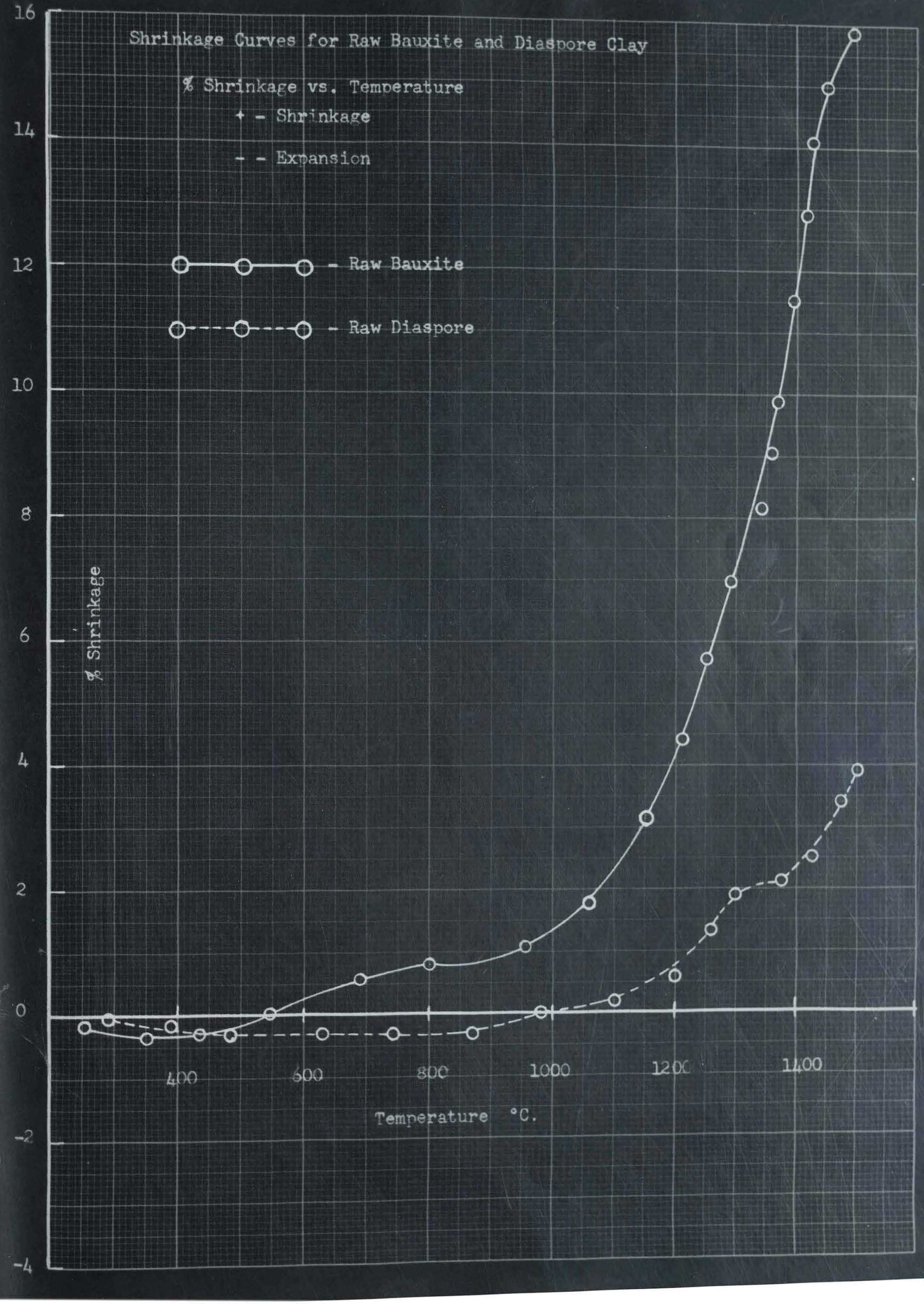
It is seen from the shrinkage curves of raw bauxite and diaspore clay that shrinkage occurs continuously up to 1400°C. At about 1500°C, there is a tendency for the slope to slightly level off. Thus it is indicated that up to 1500°C, all the shrinkage of diaspore or bauxite is not completely removed. The initial expansion is the usual expansion which has occured before the actual shrinkage is effected due to heat treatment. The breaks in the curve indicate the beginning of the removal of combined water which progresses as the temperature is elevated.

X-ray Examination

Other factors which might affect changes in the brick during the reheat test are crystal growth, development of glassy phase or new crystalline minerals, mineralization and others. Sometimes the size of the crystal originally present also grows. For identification of such developments, the x-ray diffraction method of investigation is the best one though it also presents some limitations.

A geiger counter x-ray spectrometer shown in figure 6 supplied by North American Phillip Co. was used to make the diffraction patterns of the bricks. X-rays generated from the tube pass through a collimating slit and fall on the sample mounted in a rotating sample holder. The diffracted x-rays are then received in a gieger counter, and through an amplification system are recorded on a moving chart. The gieger counter is mounted on an arc which is divided into 90° and is moved along the arc by an electric motor. As the sample moves by an angle equal to θ, the gieger counter will move by 2θ. Thus all the diffracted rays between angle 0° to 90° are picked up.

Fig. 6: Phillips North American Electric Co.'s Gieger Counter X-ray Spectrometer.


Shrinkage Curves for Raw Bauxite and Diaspore Clay
% Shrinkage vs. Temperature
+ - Shrinkage
- - Expansion
Raw Bauxite
Raw Diaspore
% Shrinkage
Temperature °C.
16
14
12
10
8
6
4
2
0
-2
-4
400
600
800
1000
1200
1400

The motion of the gieger counter is synchronised with the motor driven chart on which the intensities of the diffracted rays are plotted. If the diffracted rays are stronger, a tall peak will be recorded on the chart.

A representative sample of the brick was taken from the center as well as from the ends. The sample was then crushed in a porcelain mortar and was ground through 200 mesh. The sample was mounted in the sample holder and the x-ray diffraction patterns was made. The sample was rotated so as to avoid any preferred orientation. Such diffraction patterns were made of the calcined materials, the bricks prepared from the calcined materials and the bricks after reheat at 1400°C and 1600°C. The diffraction pattern on the chart shows intensity plotted against twice the Bragg angle θ.

In the following few pages, are shown illustrations of these diffraction patterns. On each page there are six diffraction patterns arranged in a column, each one being of a different specimen, but containing the same calcined material. Each page therefore represents the patterns for bricks before and after reheat of a particular calcined material. The calcination temperature of each material is indicated at the top of the page.

The patterns are arranged in the following order. The upper pattern is that of the calcined material which is specified on the page. The next one is for the brick which is prepared using this calcined material. The next two patterns are those for the same brick after reheat at 1400°C and 1600°C respectively. The two lower patterns are those for pure alumina and mullite. Such an arrangement of illustrations was preferred so that changes due to different heat treatments could be easily recognised and compared. The alumina and mullite patterns are placed at the bottom so that it would be easy to locate respective peaks of alumina and mullite on the brick diffraction patterns.

It may be noted from all these illustrations that a distinct change in heighths of the diffraction peaks is taking place as the firing temperatures are varying. The heighths of the peaks indirectly refer to the amount of the substance present and give proportional comparison with other substances. In all the calcined material patterns there are strong peaks for corundum indicating that a maximum amount of corundum is present. A small amount of mullite is also indicated. When the brick containing this calcine is examined, it showed further development of mullite and a decrease of the corundum peaks, though the change is not very great. This brick on further reheating, distinctly shows that more mullite growth has taken place and the amount of corundum is decreased. These changes are very apparent from the patterns, and clearly show the progressive mineral changes taking place during heat treatment. The significance of these changes and their relationships with the expansion data obtained on reheat will be discussed in detail in the next section.

BAUXITE CALCINED AT 1400°C.

Calcined Material

Brick

Brick after reheat at 1400°C.

Brick after reheat at 1600°C.

Corundum

Mullite

Fig. 8:

BAUXITE CALCINED AT 1500°C

Calcined
Material

Brick

Brick after
reheat at
1400°C

Brick after
reheat at
1600°C

Corundum

Mullite

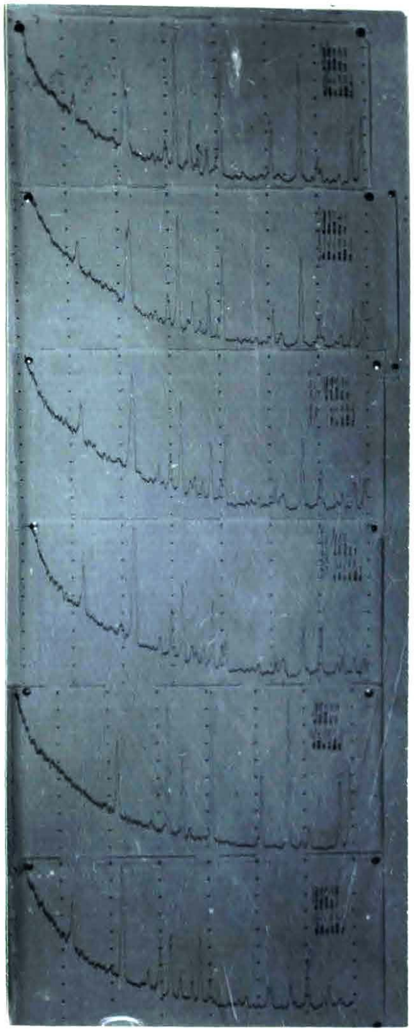


Fig. 9:

BAUXITE CALCINED AT 1600°C

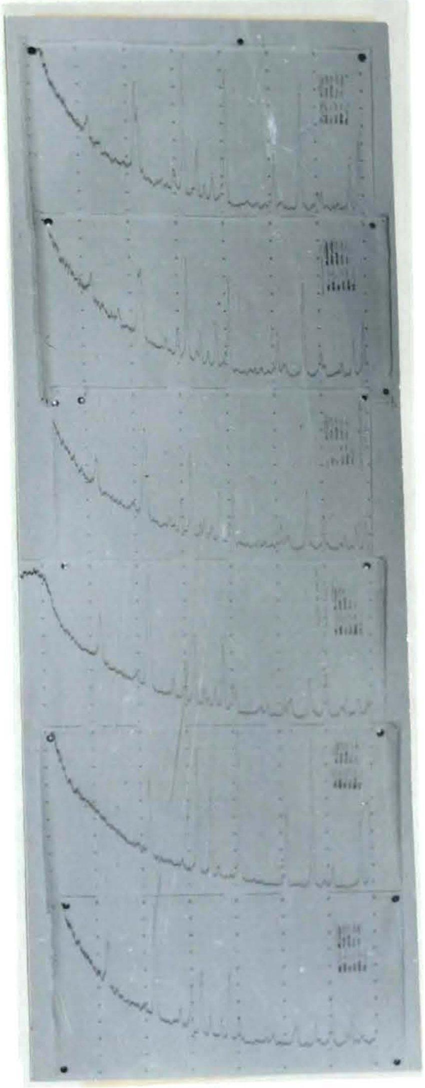


Fig. 10:

DIASPORE CALCINED AT 1400°C

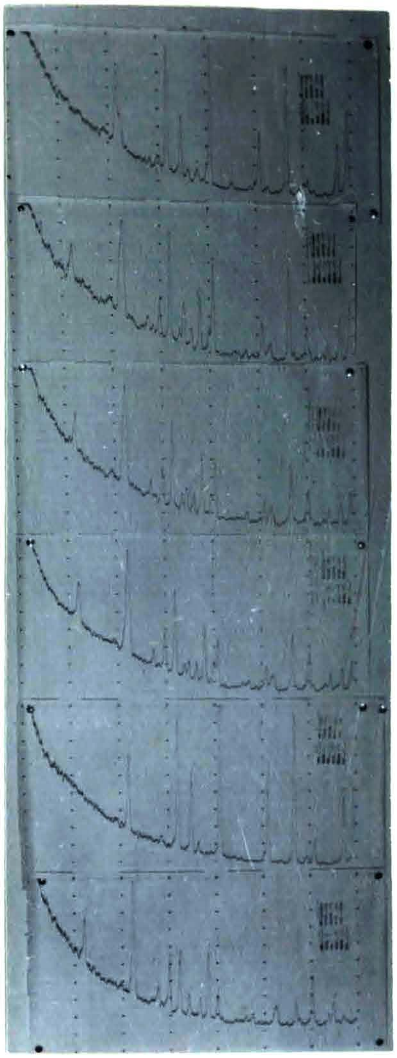


Fig. 11:

DIASPORE CALCINED AT 1500°C

Calcined Material

Brick

Brick after reheat at 1400°C

Brick after reheat at 1600°C

Corundum

Mullite

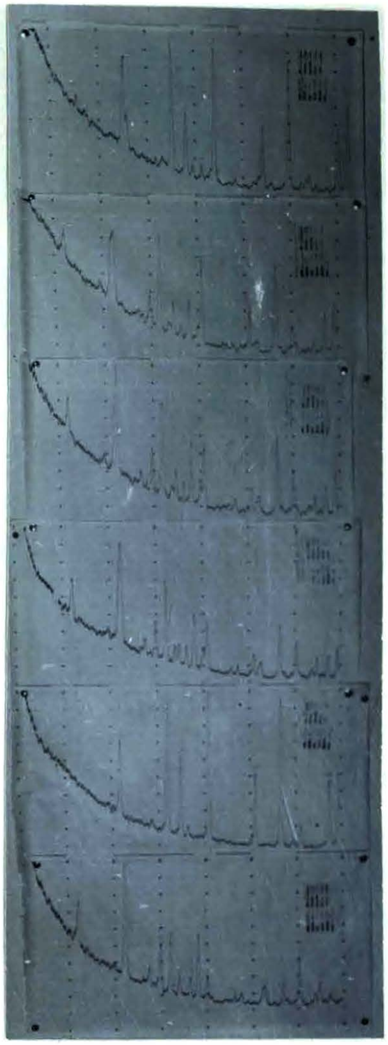
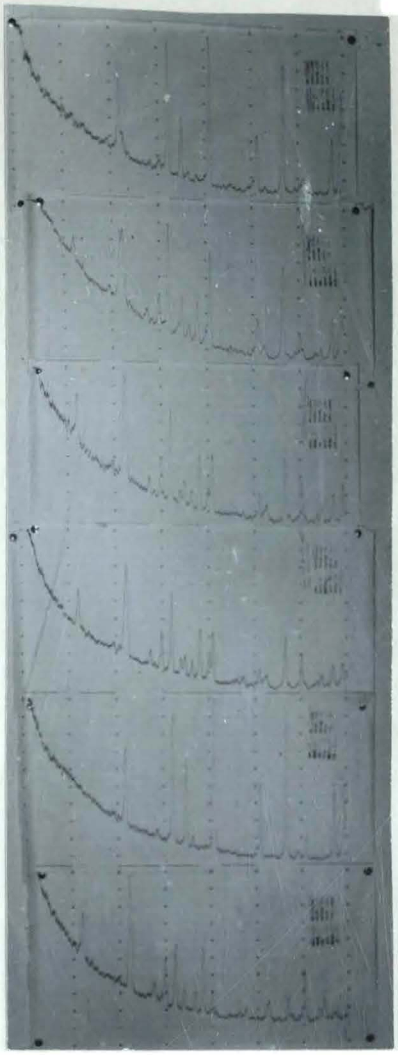


Fig. 12:

DIASPORE CALCINED AT 1600°C



Calcined Material

Brick

Brick after reheat at 1400°C

Brick after reheat at 1600°C

Corundum

Mullite

Fig. 13:

Petrographic Examination

Another technique commonly used for the identification of mineral changes in ceramic bodies is the use of a petrographic microscope. Changes which are not indicated by the x-ray diffraction method would be easily observed by a petrographic microscope. The increase in size of the crystal is very difficult to interpret from x-ray diffraction pattern unless the size is unusually small, but by microscopic examination, the changes in the size can be seen and a progressive study can be made. Also reactions taking place between the grog and the bond clay, and the way in which it progresses would only be revealed by microscopic studies. Also the void structure, and particle size distribution of the grog can be studied. Thus petrographic examination is complementary to x-ray diffraction methods of investigations and no investigation would be complete using one method without the other.

Thin sections of bauxite and diaspore bricks were made. Also thin sections were made of the bricks after reheat test at 1400°C and 1600°C. The photomicrographs shown on the following pages indicate the progressive reactions between the grog grain and bond clay as well as the reactions taking place throughout the grains themselves. The growth of mullite crystals is very conspicuous on some of the photomicrographs. The mineral changes and the relationship to the expansion caused during reheat are discussed in detail in the next section on discussion of data.

Figure 14 to 31 show photomicrographs of bricks before and after reheat, using calcined bauxite and diaspore clay. All photomicrographs are taken without Cross Nicols. Magnification is 30X.

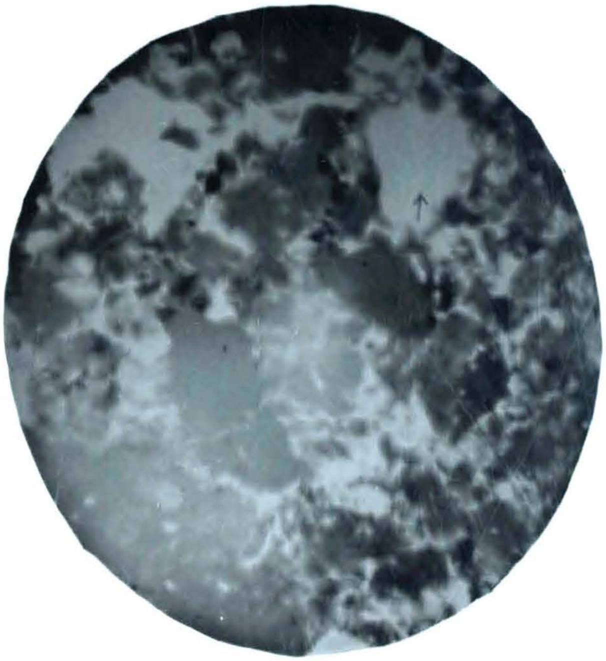


Fig. 14:

'A' - Bauxite brick with bauxite calcined at 1400°C. Arrow shows the quartz grain. Large grog grains are distinctly seen surrounded by bond clay.

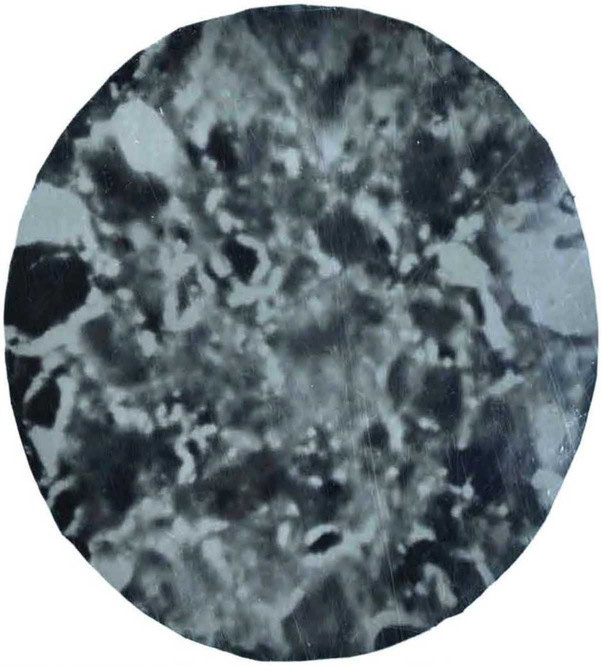


Fig. 15:

Brick 'A' after reheat at 1400°C. More reaction between grog and bond clay can be noted.

Fig. 16:

Brick 'A' after reheat at 1600°C. Dark shaded grog grain show development of mullite. Small white pin holes show minute crystals of mullite

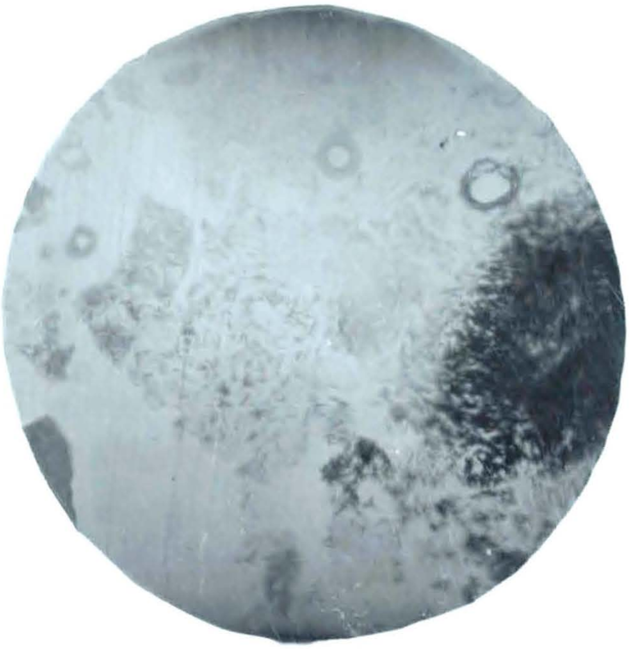


Fig. 17:

'B' - Bauxite brick with bauxite calcined at 1500°C. Arrow at right hand corner points the quartz grain.

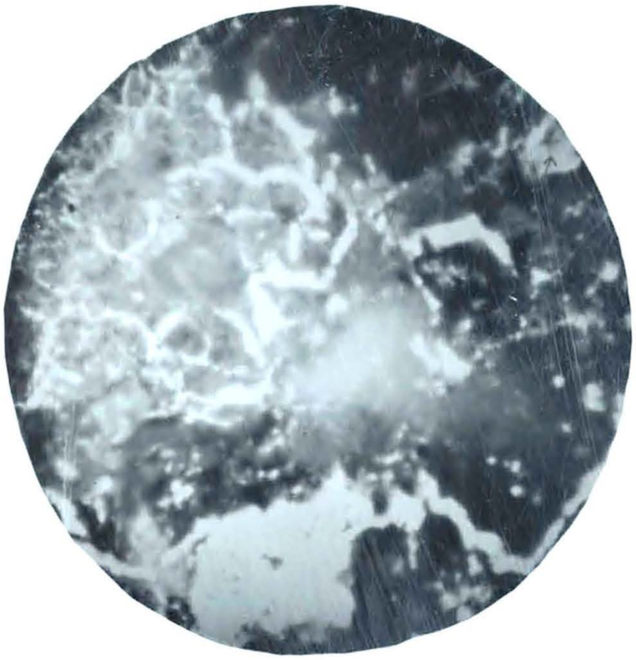


Fig. 18:

Brick 'B' after reheat at 1400°C. Arrow point the area where β-alumin development has started.

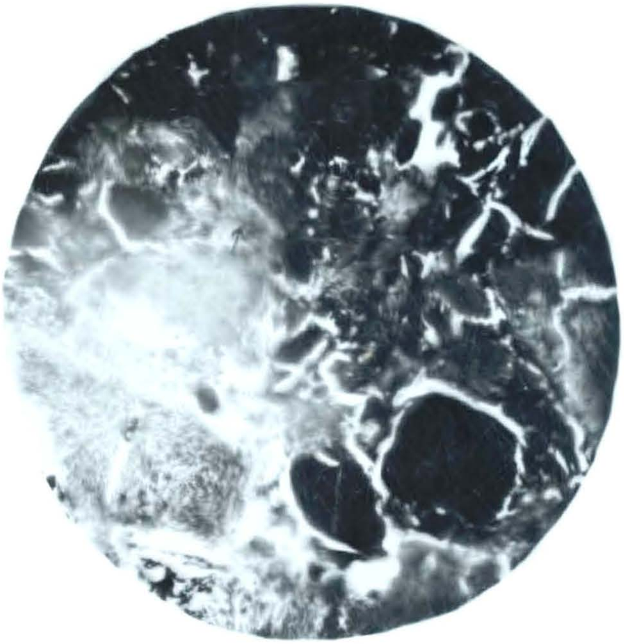


Fig. 19:

Brick 'B' after reheat at 1600°C. Arrow points a big area of β-alumina development.

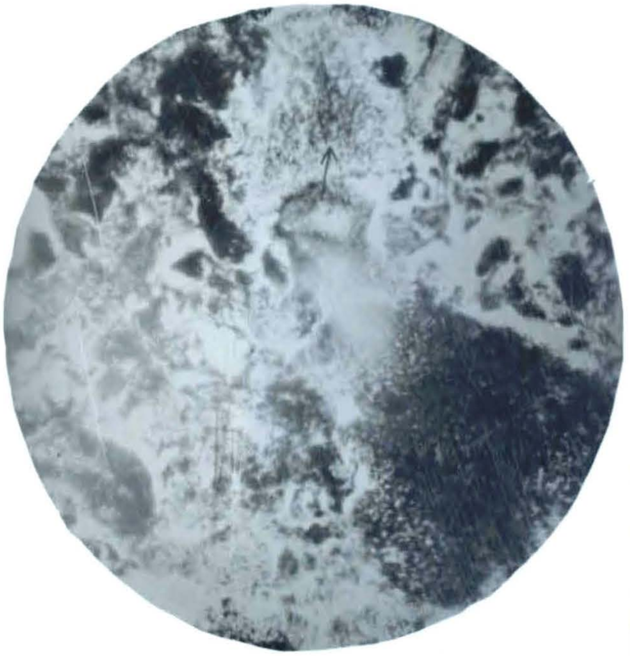


Fig. 20:

'C' - Bauxite brick with bauxite calcined at 1600°C. Arrow show the quartz grain. Some grog grains show reaction between the grain and bond clay. Black area is grinding material imbedded in thin section.

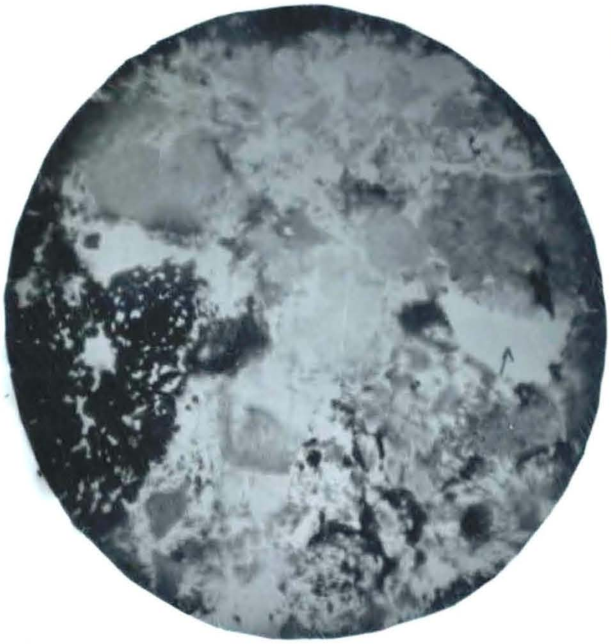


Fig. 21:

Brick 'C' after reheat at 1400°C.

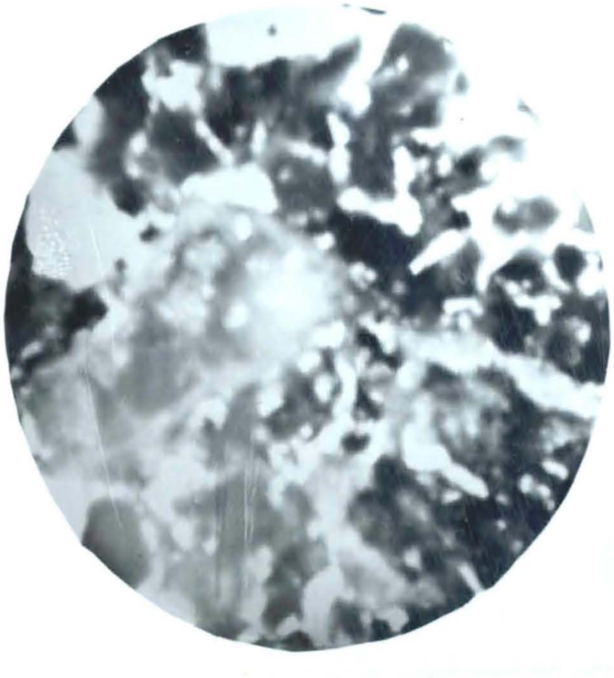


Fig. 22:

Brick 'C' after reheat at 1600°C.

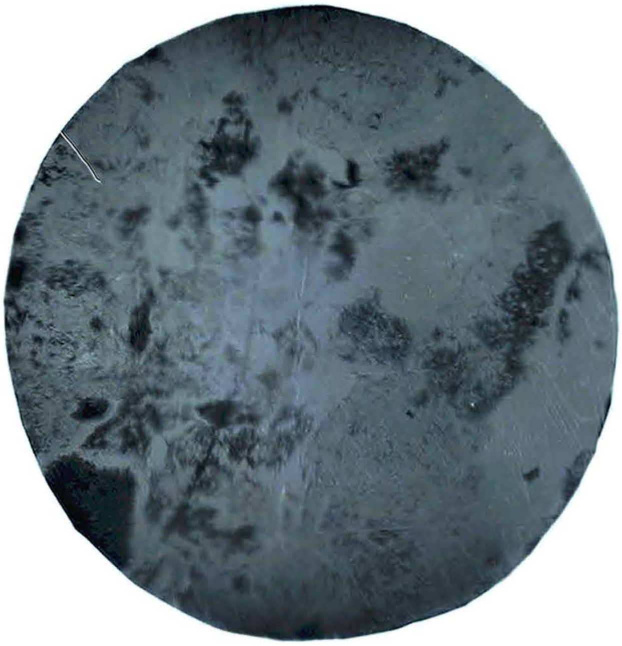


Fig. 23:

'D' - Diaspore brick with diaspore calcined at 1400°C.

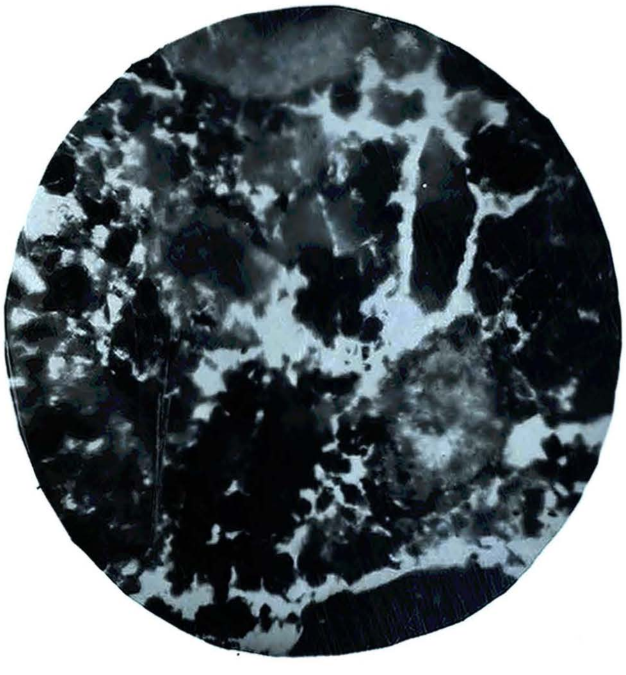


Fig. 24:

Brick 'D' after reheat at 1400°C.

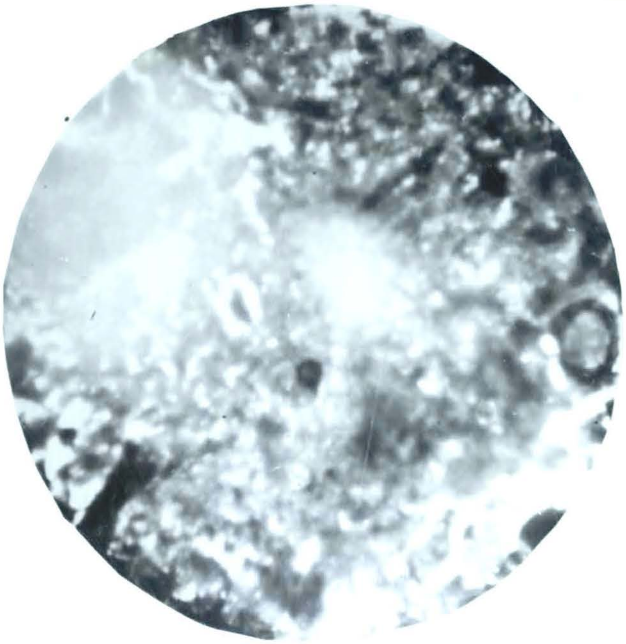


Fig. 25:

Brick 'D' after reheat at 1600°C. Progressive crystallization of mullite can be seen on each grain.

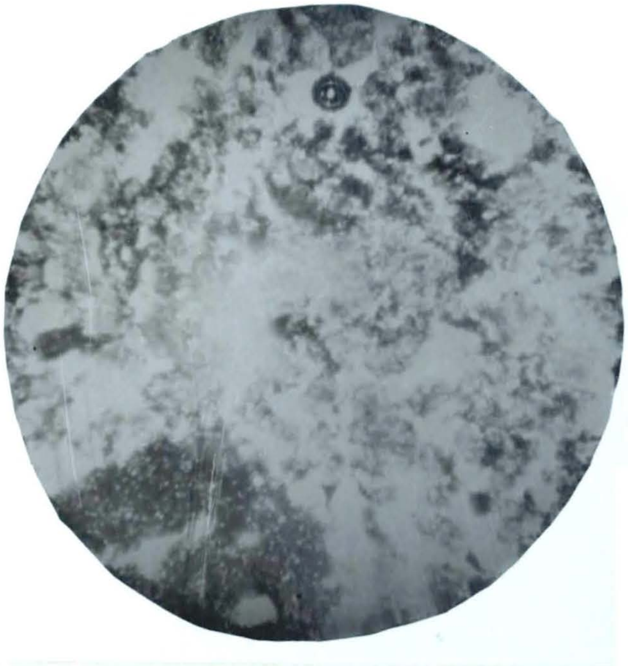


Fig. 26:

'E' - Diaspore brick
with diaspore calcined
at 1500°C.

Fig. 27:

Brick 'E' after reheat
at 1400°C. White area
in center is void space
between two big grog grains.

Fig. 28:

Brick 'E' after reheat at 1600°C. Lots of mullite crystallization is seen.

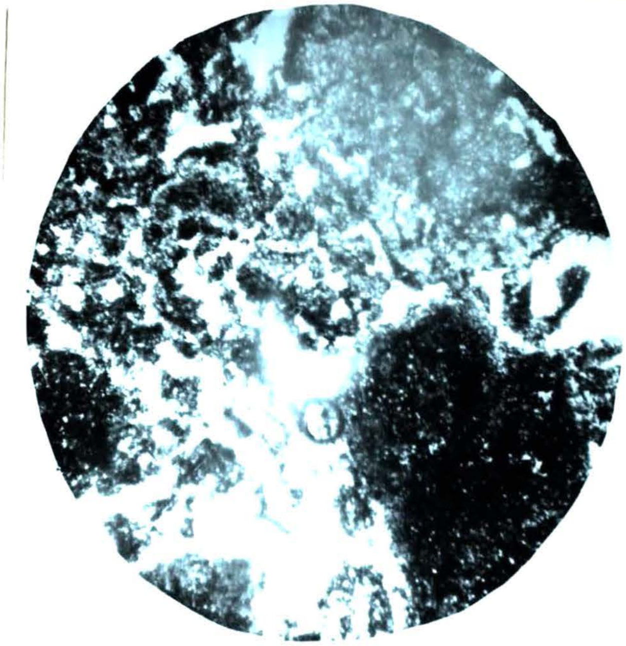


Fig. 29:

'F' - Diaspore brick with diaspore calcined at 1600°C.

Arrow points quartz grain

Fig. 30:

Brick 'F' after reheat at 1400°C.

Fig. 31:

Brick 'F' after reheat at 1600°C.

DISCUSSION OF DATA

The reheat change data show that bauxite bricks made from calcined material at low temperature (1400°C) gave shrinkage on reheat at 1400°C. As the higher temperature calcined material is used, expansion is taking place and a maximum is reached with the material calcined at 1500°C. On further increasing the temperature of calcination the expansion is reduced. Some small reheat expansion holds true with reheat at 1600°C. From the view point of effect of temperature on reheat change, all the bricks have definitely more expansion at 1600°C than at 1400°C.

As far as calcination temperature of diaspore clay, and reheat of those bricks at 1400°C is concerned, they follow the same pattern as the bauxite bricks. Low temperature calcined materials show little expansion which increases as the calcination temperature is increased. A maximum is reached for the 1500°C material, but when calcination temperature is further increased, the previous expansion is lowered to some extent. The effect of change in reheat temperature is quite different. With diaspore bricks when lower temperature calcined material is used, they show considerable expansion when reheated at 1600°C, but expansion is reduced as the calcination temperature is increased and finally shows shrinkage with the material calcined at 1600°C.

The data from the apparent porosity determinations does not contribute much to the explanation of the changes noted above on reheat. One fact is clear from these data that in cases where expansion has occurred, it has generally been accompanied by an increase in apparent porosity. This would be evident from the fact that as the calcination temperature is increased, the size of corundum grain is increased as well as some mullite growth also might have taken place. This means that more space will be occupied by large crystals of corundum and will be interlocked with the mullite crystals arising at the interface between the grog and bond clay. Furthermore shrinkage at higher temperature reheat with decrease in porosity, might be attributed to the formation of a glassy phase which might have occupied the pore spaces. This is not observed from the petrographic examination although the growth of mullite crystals are very clearly seen in the photomicrographs. The decrease in porosity and increase in mullite growth on increasing the temperature might be related with each other in this manner. As the size of mullite crystals is very minute and they are needle-like in shape, they will arrange themselves and will become closely packed between the pores and this might cause shrinkage as well as a decrease in porosity.

This does not explain perfectly the phenomena because, as the mullite is increased, the lower density material is being increased in the brick and eventually this should cause expansion.

X-ray diffraction data gives much information on the growth of mullite as well as of the corundum. The diffraction patterns have peaks for both mullite and corundum and some places on the patterns both peaks occur at the same angle and the high intensity of the line may be the combined effect of both these crystals. To get clear and unaffected peaks, the independent intensity peaks of the corundum and mullite are selected at the angle 2θ of 53 1/2° and 52° respectively. With the same setting on the spectrometer, the intensities of these corundum and mullite lines were recorded for all bricks before and after reheat. These peaks are shown in figure 32 .

Starting from right to left, the first three sets of peaks are for bauxite brick having calcined bauxite at 1400°C, 1500°C and 1600°C respectively. There follows, peaks for the diaspore bricks containing diaspore calcined at 1400°, 1500°, and 1600°C. For each set of peaks, the left hand peak is for mullite, while the right hand peak is for corundum. Between these two peaks, adjoining the corundum, there is another small peak which is for mullite, and should not be considered at all for comparison. From the graphs it will be clearly seen that the heighth of this peak is increasing along with the increase in size of the other strong mullite peaks used for comparison. Reading from top to bottom, the pattern for brick is at the top and is followed by the bricks after reheat at 1400°C and 1600°C respectively.

The heighth of the peak is a direct measurement of the amount of crystals present. This is not true always, but when only two phases of crystals are considered it gives a very good comparison. Therefore the heighths of all these peaks are measured in units of the divisions on the graph and are recorded in Table XIII.

TABLE XIII

Observations From the X-ray Diffraction Data

Amount of Corundum -

	A	B	C	D	E	F
Brick	5.6	4.8	4.9	5.1	4.7	5.3
R. H. at 1400°C	2.8	3.3	3.0	3.2	3.5	3.4
R. H. at 1600°C	1.1	1.8	1.2	2.7	2.6	2.9

Amount of Mullite -

	A	B	C	D	E	F
Brick	2.9	2.5	2.4	3.0	2.3	2.4
R. H. at 1400°C	3.5	3.1	3.0	3.1	3.4	3.2
R. H. at 1600°C	3.9	4.1	3.9	3.1	3.3	2.8

A - Bauxite calcined at 1400°C
B - Bauxite calcined at 1500°C
C - Bauxite calcined at 1600°C
D - Diaspore calcined at 1400°C
E - Diaspore calcined at 1500°C
F - Diaspore calcined at 1600°C.

Brick

Brick after reheat
at 1400°C

Brick after reheat
at 1600°C.

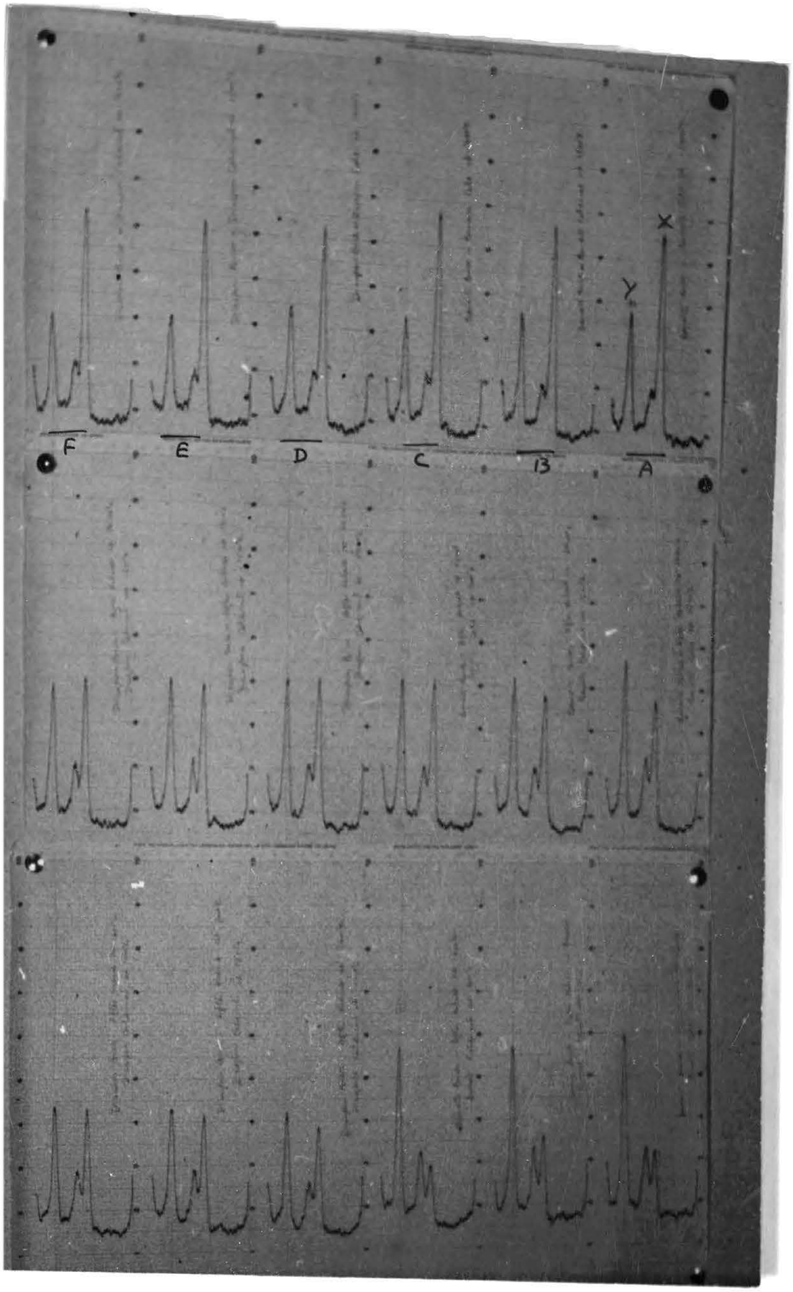


Fig. 32: Comparison of amounts of corundum and mullite in bricks before and after reheat at 1400° and 1600°C by x-ray diffraction method. The heights of each peak is an indication of amounts present. Peak 'X' of the set is for corundum and 'Y' is for mullite. A, B, and C represent the bricks made by using bauxite calcined at 1400°, 1500° and 1600°C respectively. D, E and F represent the diaspore bricks having diaspore calcined at 1400°, 1500° and 1600°C.

These data indicate that in bauxite bricks initially there is more corundum present than diaspore bricks. There is not an appreciable difference in the amount of mullite present in both these bricks. One fact may be noted in these bricks that the amount of corundum is a little less in the bricks having 1500°C calcined material as compared to others. As the bricks are reheated at 1400°C, the amount of corundum is decreased in all the bricks while the amount of mullite is comparatively increased. On further reheat at 1600°C, the corundum is further reduced. Bauxites bricks after reheat at 1600°C, have much less corundum as compared with diaspore bricks. Mullite has increased on further reheat, but bauxites bricks have much more mullite than diaspore bricks. This is evident from the fact that corundum is less and therefore must have more mullite, in bauxite bricks.

The effect of calcination temperature on the amount of corundum and mullite present after reheat is considered next. It is difficult to make a comparison in this respect, but a few distinct features can be easily observed. In the original fired bricks, the amount of corundum is less in bauxite and diaspore bricks containing 1500°C calcined material, but on reheating these bricks, the amount of corundum present is much more as compared to the other bricks after reheat. On reheating at 1600°C, 1500°C calcined bauxite has a larger amount of corundum. For the same type of diaspore bricks this difference is not as distinct. The mullite is growing on increasing reheat temperature, but there is not a very distinct comparison as far as calcination temperature is concerned, In bauxite bricks irrespective of calcination temperature the amount of mullite is practically the same. Diaspore bricks also exhibits such a relationship although the highest temperature calcined material has a lower amount of mullite.

From the x-ray data, the maximum expansion of the bauxite brick containing bauxite calcined at 1500°C, on reheat at 1600°C, may be attributed to the maximum amount of mullite present along with a higher amount of corundum. Also in the 1400°C reheat bricks both mullite and corundum are higher than in the other bricks. This is not true at some of the other temperatures. For example, the diaspore brick containing diaspore calcined at 1400°C and reheated has considerable expansion. It has, however, a less amount of mullite and corundum then the diaspore brick containing 1500°C calcined material. Therefore, more information is necessary besides that obtained from x-ray. This information can be obtained from the petrographic study.

The photomicrographs of all bauxite and diaspore bricks show large grog grains surrounded by bond clay which is light in color. The areas much lighter in color are voids. All these microphotographs of bricks also show the presence of quartz crystals. These are printed out on the pictures. These quartz crystals must have come from the plastic fire clay used as a bond. It may be noted that this plastic fire clay contains small amounts of free silica, which fact has been pointed out in the discussinn of raw materials.

A systematic study of the changes taking place in a brick on reheat, will be made. Bauxite bricks prepared containing 1400°C calcined material show large grog grains surrounded by bonding, No distinct reaction between the grains and bond clay, or within the grain can be seen. The grog grains are much darker in color. On reheating the brick at 1400°C, a reaction at the edges of the grog grains can be seen in the form of light shaded rings surrounding the grain. Still the reaction within grog grain has not started. On further reheat at higher temperature, the rings have disappeared and much faint colored area is left around the grain. Each grog grain is distinctly attacked throughout its mass and the small white dots are due to growth of minute mullite crystals. Another grain besides can be seen having the reaction just started. Thus this brick shows growth of mullite on reheat.

Bauxite brick containing bauxite calcined at 1500°C shows large grog grains surrounded by the bond clay, having few quartz crystals as impurity. On reheating this brick at 1400°C, some grains are much more attacked and a considerable amount of mullite is formed. On this photomicrograph new crystal growth is observed which is dissimilar to the mullite. Though it is found in very small amounts it is very conspicuous. These crystals are found to be β-alumina. On the photomicrograph these crystals are pointed out by the arrow. This growth of β-alumina is very distinctly seen on the microphotograph of the brick after reheat at 1600°C. The difference between the crystals of mullite and β-alumina on the photograph is that, the grains having growth of mullite are much darker and have white pin holes or spots on the grain, while β-alumina as pointed out does not exhibit such characteristics.

Brick containing 1600°C calcined bauxite show grains having some initial reaction due to higher calcination temperature. Nothing much can be said about the effect of increasing the reheat temperature except that at higher temperature reheat all grog grains show the mullite crystal growth.

Diaspore bricks containing materials of various calcination temperatures follow the same trend. In these bricks each grog particle is separately seen, but on reheat, the reaction between the bond clay and grog as well as within the grog grains starts and is just about completed on further reheat at higher temperatures. All diaspore bricks after reheat at 1600°C show a very intense growth of mullite.

Much more important information thus is collected from the petrographic study. Especially the unusually high expansion of the bauxite brick containing the 1500°C calcined bauxite can be more easily understood. The presence of β-alumina would certainly cause an expansion of the brick. This can be seen by comparing the size of the unit cell of corundum (α-alumina) with that of β-alumina. The corundum is a hexagonal close packed arrangement of aluminum and oxygen atoms having a unit cell 4.75 A.U. by 13.02 A.U. The β-alumina is a hexagonal compound composed of sodium or potassium, aluminum, and oxygen in the ratio of 5.2% Na_2O or K_2O to 94.8% aluminum oxide. The unit cell is 5.56 A.U. by 22.55 A.U. Thus when a small amount of soda or potash combines with α-alumina at high temperatures the crystal expands by 175% in one direction and 12% in the other direction.

CONCLUSIONS

The amount of mullite present in the brick would generally cause the expansion of the brick as the former material has a lower density. But during this investigation discrepencies are noted in certain cases where in spite of mullite growth being equal in amount, the bricks exhibit differences in expansion behavior.

The amounts of mullite and corundum in bauxite bricks containing bauxite calcined at 1500°C and 1600°C, is nearly the same, but the former has much more expansion than the latter. Therefore, this criterion does not explain the cause of unusual expansion of the bauxite brick made with material calcined at 1500°C.

This expansion can be attributed to the presence of β-alumina, which was observed in this brick during the petrographic study. This β-alumina is formed by reaction of α-Al_2O_3 with alkalies present in the bond clay. The bond clay is higher in alkali content, and if all the alkali content of bond clay in the batch is utilized in formation of β-alumina, enough β-alumina will be formed to cause at least more than 1% expansion. This is calculated on the basis of the amount of β-alumina which would be formed and the effective increase in size calculated from the lattice constants ratio.

The next question which arises in this connection is: as bauxite itself has low alkali content, and all the bauxite bricks have the same amount of bond clay, why does not such a reaction take place in the case of the other two bricks?

Bricks containing 1400°C calcined bauxite might react with alkali to form β-alumina, but it has got such an excessive shrinkage on reheat that the expansion effect, if any, might have been overlapped. This shrinkage occurs as the initial low temperature of calcination (1400°C) is not enough to remove all the shrinkage from the bauxites. This fact is noted from the shrinkage curve of raw bauxite and the expansion curve of the bauxite bricks. At higher temperatures the β-alumina would be decomposed to α-Al_2O_3 and alkalies would be given out, as alkalies are very volatile at higher temperatures. Also alkalies fit into the holes of the lattice structure and are loosely bonded so that with little effort at higher temperature they can be removed. Therefore bauxites bricks containing 1600°C calcined material after reheat at 1600°C, do not show any presence of β-alumina.

The next point is why such a reaction is not noted in diaspore bricks. Here the attention is drawn to the batch composition of the brick. As both diaspore and bauxites are calcined, there is little chance that very much alkali would be left after the calcination treatment, but the only alkali contributed would be from the bond clay. The batch for bauxite brick calls for larger amounts of bond clay than the batch for diaspore and therefore eventually the bauxite bricks would have more alkali for reaction. As far as the effect of reheat temperature is concerned all reasoning given for bauxite bricks could safely be applied. Thus it can be distinctly shown that the expansion of the bauxite brick containing bauxite calcined at 1500°C, is due to the development of β-alumina.

If it is necessary to use bauxite for making a high alumina brick having a good volume stability, the bauxite must first be calcined at 1500°C for the high alumina grog. This grog is then blended with a small amount of diaspore grog made by calcining diaspore clay at 1500°C. Thus the amount of bond clay required will be lessened and such a brick would not show any changes on reheat. In this way the use of diaspore clay can be reduced to a minimum and be effectively displaced by bauxite. The exact batch would be more or less a matter of adjustment for the required volume stability.

SUMMARY

The high alumina grog is prepared by calcining bauxite and diaspore clay at 1400°, 1500° and 1600°C. High alumina (70%) refractory bricks are made using this grog and plastic fire clay as a bond. Bricks are fired to cone 15 down, and are then subjected to reheat test at 1400°C and 1600°C. The bauxite brick with bauxite calcined at 1500°C showed unusual expansion, as compared with reheat changes on other bauxites and diaspore bricks. By x-ray and petrographic study it was observed that this expansion is caused by the development of β-alumina. Finally recommendations are made as to how the bauxite can effectively replace the diaspore clay for manufacturing high alumina (70%) refractory bricks.

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VITA

BHIKHUBHAI MAHADEO SEDALIA, the second son of Mahadeo Oghad, was born on April 7, 1923, at Godhra in Bombay province, India. He attended the New High School at Godhra and passed the requirements of Matriculation examination of Bombay University in 1938. He attended Baroda College at Baroda and RamNarain Ruia College at Bombay and received his Bachelor of Science degree with Chemistry major, from Bombay University in 1942.

Just after the graduation, he joined the war services and was appointed as an analytical chemist to Ordnance Laboratories of Indian Army Ordnance Corps, under defense ministry of Govt. of India. These laboratories are now known as Technical Development Establishments, under directorate of technical developments. During the service, he was also partly attached to Central Medical Laboratories of Govt. of India. In April 1949, he resigned his duties for sake of further studies and got discharge with rank of supervisor.

With private help of Mr. P. J. Gohel, he ventured for higher studies and left India for United States of America on May 23, 1949. He arrived in New York on June 20, 1949

He entered Missouri School of Mines in September 1949 as a graduat student for the degree of Master of Science in Ceramic Engineering. During the study, he worked as Chemist to Missouri Clay Testing and Research Laboratories from Feb. 1950 to July 1950. Since September 1950, he is a 'Graduate Assistant' in Ceramic Engineering Department.

He is an active member of Keramos fraternity and student member of the American Ceramic Society.