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THE TESTING OF CLAY REFRACTORIES, WITH SPECIAL REFERENCE TO THEIR LOAD CARRYING CAPACITY AT FURNACE TEMPERATURES

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Bureau of Standards

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By A. V. Bleininger and G. H. Brown

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1. OBJECT OF WORK

This paper deals with the general question of the refractoriness of the so-called fire clays and, in connection with this, their viscosity at furnace temperatures. The viscosity is an important factor in the behavior of fire brick and other clay refractories under the load conditions which prevail in industrial furnaces. While the loads imposed may be slight and would be insignificant as far as the strength of the product in the cold condition is concerned, they become an important factor at elevated temperatures. Thus, while a fire brick may show a compressive strength of 2500–3000 pounds per square inch at atmospheric temperature, it will possess but a small part of this strength at a temperature of, say, 1300° C.

This decrease in resistance to deformation has a more important bearing upon the durability of refractories than is generally realized. Conditions of strain prevail in almost any part of a furnace, especially in crowns, bridge walls and bags, checkerwork, retort benches, muffles, etc. To these must be added the strains imposed by expansion and contraction due to temperature changes and those due to other causes. The loss in resistance to compression is evidently due to the lowered viscosity, caused by the gradual softening of the clay due to vitrification and incipient fusion. This viscous state becomes more and more prominent as the temperature rises until the point is reached when the material can no longer support its own weight. The rate at which a clay approaches this semiliquid state with increasing temperature may be said to be roughly proportional to the rate of vitrification, i. e., the speed with which the pore space closes up due to partial fusion. The contraction is the result of surface forces tending to reduce the area of the body to a minimum.

A fire-clay body low in fluxes, i. e., titanium oxide, ferric or ferrous oxide, lime, magnesia, potash and soda, showing a low rate of vitrification will consequently be affected less under furnace conditions with increasing temperatures than one higher in basic constituents.

In this work have been considered the conditions under which the refractoriness of clays is reduced, as well as the means avail-

able for differentiating between high grade and unsatisfactory products by means of laboratory tests.

As has been stated in the title, the work has been confined to fire-clay bricks, and the treatment of silica and magnesite bricks and other refractories has not been undertaken.

2. NATURE OF REFRACTORY CLAYS

(a) **Chemical Composition.**—The principal ingredient of fire clay is a hydrous silicate of alumina, of the formula $Al_2O_3 . 2SiO_2 . 2H_2O$, corresponding to the following percentage composition:

	Hydrous	Dehydrated
	Per cent	Per cent
Silica	46.3	53.8
Alumina	39.8	46.2
Combined water	13.9	....

While this substance, commonly called kaolin, does not correspond to the most refractory mineral combination of silica and alumina found in nature, it is at least the most commonly distributed material, since it may be assumed to be the fundamental constituent of all fire clays. Other minerals, such as sillimanite, cyanite, and andalusite, corresponding to the general formula $Al_2O_3 . SiO_2$, are far more infusible, but are of comparatively rare occurrence in clays.

The so-called melting point of pure clays is close to that of platinum; that is, about 1755° C. Substances whose softening temperatures differ too greatly from that of kaolin should not be considered as fire clays. Though the chemical composition of fire clays approaches more or less closely that of kaolinite, $Al_2O_3 . 2SiO_2 . 2H_2O$, they differ widely as regards their physical structure, varying through all stages from the well-defined crystalline state to that of a typical colloid. From the technical standpoint, roughly, three classes of refractory clays may be distinguished, viz, kaolin clays, flint clays, and plastic clays.

(b) **Kaolins.**—The first class of materials, usually of geologically primary origin, consists, in the purified state, of white clayey

matter, containing both the crystalline and amorphous varieties of clay base. In some of these clays the crystalline constituents predominate, as in the North Carolina kaolins. The plasticity of these clays is but feebly developed, though where the granular matter has been broken down by the action of water or other agencies to the amorphous condition, a fair working quality may result. These clays, on account of their whiteness, are used in the pottery industries.

There are, however, kaolins which possess a good degree of plasticity, as the Georgia kaolins and some of the English china clays. These, as long as they maintain good whiteness, are highly valued in the manufacture of white ware and porcelain products. Frequently, however, increased plasticity is coincident with increased content of fluxes and consequent reduction in refractoriness. While marked plasticity in itself, of course, does not mean reduced refractoriness, it indicates geological conditions which tend to incorporate impurities in the clay.

Owing to their purity (absence of basic oxides) the kaolins are the most refractory clays. Thus a well-known kaolin from Zettlitz, Bohemia, which is considered a standard material of its kind, shows a softening temperature corresponding to Seger cone No. 35, estimated to correspond to a temperature of 1755° C, according to the scale adopted by the Bureau of Standards (palladium = 1549° C; platinum = 1755° C).

(c) **Flint Clays.**—The so-called flint clays embrace many materials of a grade of purity corresponding closely in composition to the best grade of kaolins. Like the latter, they may, of course, deteriorate into clays of comparatively low refractory value. As has been said, their composition is very close to that of the kaolins, even as to the content of chemical water. Physically they are unlike the soft and chalky kaolins in possessing a hard, dense amorphous structure, showing a peculiar well-defined conchoidal fracture. The color is usually gray. The initial plasticity is exceedingly feeble, though if exposed to the weather or if ground either dry or wet the condition of colloidal "set" may be partially overcome and sufficient plasticity developed for molding purposes. Owing to the weak plasticity possessed by flint clays, their drying

shrinkage when ground and made up with water is very slight. On the other hand, in burning these clays undergo a considerable shrinkage. In this respect, however, considerable difference exists between the various materials, apparently dependent upon the colloidal state of the clay base. Thus, for instance, a Pennsylvania flint clay from Clearfield County showed a linear shrinkage of 5.5 per cent up to cone 20; a Maryland clay of the same type was found to possess a maximum shrinkage of 5.6 per cent at cone 11, which decreased on further heating to 3.5 per cent at cone 20, indicating an increase in volume; a Kentucky flint clay, on the other hand, showed a steady gain in shrinkage up to cone 9, when it reached a linear contraction of 9 per cent, while at cone 20 it showed 9.5 per cent.[1]

The volume shrinkage characteristic of these clays subjects the structure of the product into which they enter to a severe strain, which, owing to the low tensile strength, may cause serious difficulty due to cracking and checking, so that it may be necessary either to calcine the flint clay before incorporating it in the body or to replace it in part by ground waste bricks (grog).

The burning shrinkage in the case of flint clays can not be entirely attributed to the contraction accompanying vitrification. Considering the purity of these clays it is evident that part of the shrinkage is independent of this factor and must be due to a molecular change of another kind, that peculiar to many typical amorphous substances like alumina, magnesia, zirconia, etc. We may, therefore, ascribe the high-burning shrinkage of flint clays to colloidal volume changes.

In Fig. 1 the shrinkage curves of a Pennsylvania and a Ohio flint clay are given.

Geologists are not agreed as to the origin of flint clays, an obscure subject upon which definite information seems to be lacking.

Besides the flint clays proper there are certain dense fire clays of feeble initial plasticity which lack the other characteristics of this class of materials. The writers have examined such a clay occurring in Alabama which evidently had been formed under conditions radically different from those producing flint clays. Hard

[1] J. M. Knote, Trans. Am. Ceram. Soc., vol. 12; University of Illinois Bull., 7, No. 30.

nodules of amorphous silica (flint) were found to be associated with this clay, which in itself was dense, of a white color, and by fine grinding could be made to attain a good degree of plasticity. It did not represent the degree of inertness usually shown by flint clays.

(d) **High-Grade Plastic Clays.**—Clays, combining good plasticity and refractoriness, are not of common occurrence. While there are some examples of this type, the majority of the deposits

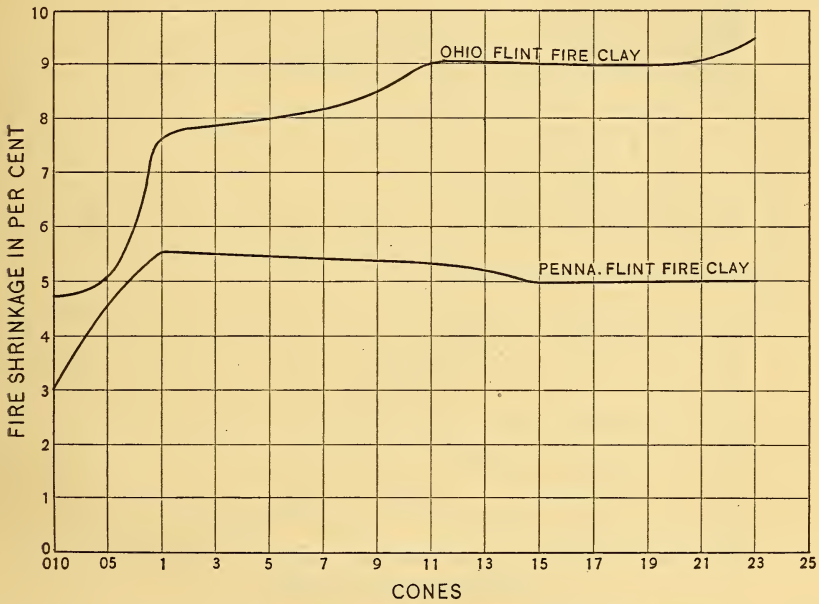

Fig. 1.—*Curves showing the fire shrinkage of two flint fire clays*

usually show plasticity at the expense of heat-resisting power, and in addition show variations in quality which render their use in the industries more or less uncertain. Some plastic clays of high grade are known as kaolins, such as the white clays from Georgia, Alabama, and Florida. Outside of these the bulk of the plastic fire clays are of carboniferous and tertiary origin. While the kaolin-like clays are not at present used to any extent in the refractory industries they could be made available as bond clays most successfully. Owing to the higher content of impurities, the plastic clays necessarily show distinct evidence of vitrification at

considerably lower temperatures than the pure fire clays. This is shown clearly in Fig. 2, where the porosity temperature curves of both flint and plastic clays are given, taken from the work of Knote.[2] Since vitrification is coincident with decrease in porosity it is evident that the slope of the porosity curve is characteristic of the refractory behavior of the clay. Pure clays, up to tem-

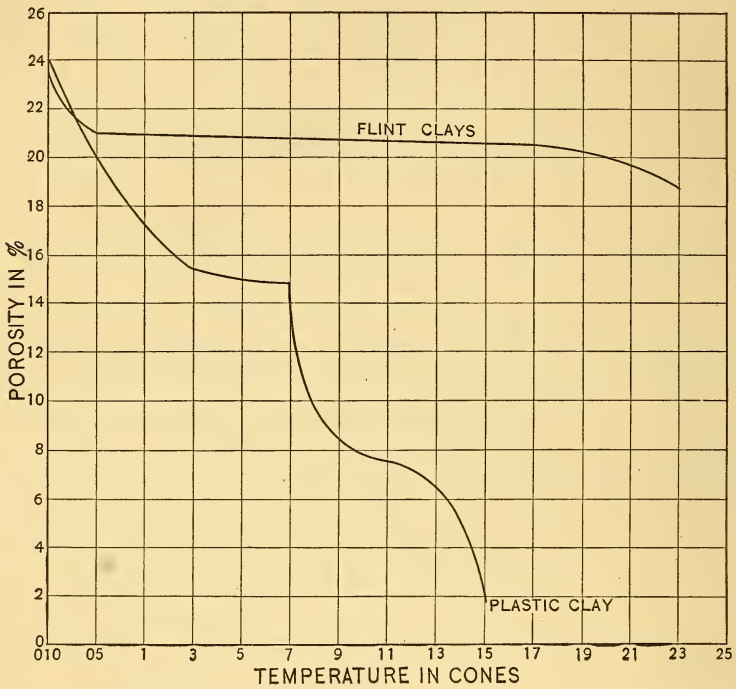

Fig. 2.—*Diagram showing relation between firing temperature and per cent porosity for a flint and a plastic fire clay*

peratures approaching the softening point, should show no marked tendency to become dense, i. e., the porosity should remain high. The lower the temperature at which the porosity of the clay becomes practically nil, the more inferior is its refractory quality. The ideal fire clay would thus be represented by a straight line along its initial porosity, beyond a temperature of about 1000° C, from which line impure materials depart, according to their content of fluxes.

[2] Loc. cit.

3. MANUFACTURE OF REFRACTORIES

The simplest case of fire-brick manufacture is that in which a highly refractory clay of sufficient plasticity can be molded into the desired shape, dried, and burnt. Since, however, this is not possible when the material is either lacking in refractory or working quality, a condition which is the rule rather than the exception, mixtures of different clays must be employed. One of the most common cases is the use of flint clay with plastic clay as the cementing agent, which produces the required working condition. The higher the grade of the latter is, as regards refractoriness, the higher, of course, will be the quality of the resulting product. Whenever it is necessary to make use of a plastic clay of inferior refractory quality it is evident that as little of it should be incorporated in the mixture as possible. A very common proportion is that of 85 per cent of flint and 15 per cent of bond clay. Such a mixture possesses sufficient plasticity to be worked by the so-called slop-mold process, but could not be molded by means of the auger machine. There is, of course, no difficulty in pressing the bricks by the dry-press process.

It is evident that when a refractory may be made of a single high-grade material, the resulting quality is bound to be better than in the case of composite bodies. It is possible to do much in this connection along the lines of developing the latent plasticity of flint clay by fine grinding and blending of the plastic clay with some flint clay, thus bringing up the heat resistance of the bonding material. The importance of the latter procedure is pointed out later in the discussion of fire-brick tests. Briefly, wherever a plastic bond clay must be employed its amount should be reduced as much as possible, unless, of course, it is a satisfactory refractory clay in itself.

4. FUSION OF CLAYS

(a) **Fusion Point.**—The fusion of even the purest clay, both in the crystalline and the amorphous condition, proceeds gradually, very much like that of quartz (tridymite), and it is erroneous to speak of a definite melting point for clay. In technical work the deformation and collapse of a specimen is usually employed as the

criterion of the fusion point. Although this has no theoretical meaning, it answers the purposes of practice. The question of viscosity enters into this consideration as well, since some silicates flow more easily than others, though heated at the same rate. Owing to the fact that the crystalline structure of kaolinite is destroyed after dehydration, we are dealing in the case of clays with amorphous substances which behave in a measure like liquids of high viscosity.

(b) **Pyrometric Cones.**—As an illustration of the determination of the so-called melting point of silicates, the Seger cones may be cited, which are small tetrahedra molded from various mixtures of kaolin, feldspar, calcium carbonate, quartz, and ferric oxide, designed to soften at regularly increasing temperature intervals. The melting point, so called, of these cones is accepted to be that temperature at which the apex of the cones touches the fire-clay tile upon which they are placed, as is illustrated in Fig. 3. These pyroscopes are largely used in the ceramic industries and offer a valuable means of controlling burning operations, since, in fact, they measure heat effect rather than temperature, which includes the factor of time. The cones have never been claimed by their originator, Dr. H. A. Seger, to measure temperatures; in fact, he strenuously opposed any such application of his device. As a matter of fact, the cones indicate temperatures with a fair degree of accuracy, considering their nature, under the same conditions of firing, though it is well understood that upon longer heating the softening point indicated is lower than upon quick heating.[3] Seger cones are generally used in testing fire clays or refractory products for heat resistance. The common practice is to place the specimen to be tested into a furnace together with a number of the standard cones, the temperature being carried to the collapsing point of the sample. After cooling the cones are inspected and the highest number which has softened and bent is considered to correspond to the "melting" point of the specimen under test. The Deville coke-fired furnace is commonly employed for this work, but the more recent electrical carbon-resistance furnaces, in which the specimens are placed within highly refractory muffles, are to be

[3] Hoffmann, Sprechsaal, 44, pp. 143–145.

preferred. These furnaces permit of the direct observation of the cones and the temperature may be determined by means of the Morse, the Holborn-Kurlbaum, or a similar optical pyrometer.

In Fig. 4 the diagram of a furnace used for this purpose in the clay-products section of the Bureau of Standards is given.

Fig. 3.—*Seger cones before and after bending*

For the purpose of comparing the softening temperatures of fire-clay specimens with those of the standard cones the numbers 26–36 are employed, while for special refractories, such as bauxite bricks, etc., the numbers 37–42 are used. The softening temperatures of the Seger cones have been determined in the Reichsanstalt by Hoffmann,[4] based upon the Holborn and Day temperature scale, the temperatures above 1150° C having been obtained by extra-

[4] Tonindustrie Zeitung, **33**, pp. 1577–1580; 1909.

polation from the emf-temperature equation of the platinum, platinum-rhodium thermocouple. On this scale the melting point of palladium is 1535° and that of platinum 1710° C. The values thus obtained should no doubt be corrected to correspond with the more recent determinations of the melting points of palladium

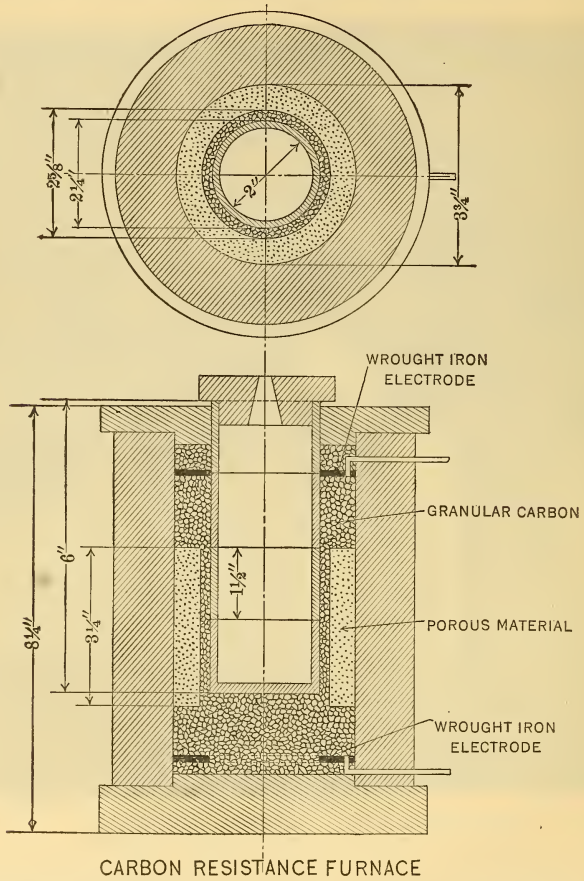

Fig. 4.—*Diagram of electric carbon resistance furnace for the determination of the softening temperatures of cones*

and platinum, which are 1549° and 1755° C, respectively. Since, after making this correction, some small irregularity occurs in the curve connecting temperature and cone number, Dr. C. W. Kanolt has suggested that a smooth curve be drawn through the points, a procedure which seems to be justified.

In the following table are compiled the compositions of the higher Seger cones, expressed in molecular equivalents, together with the softening temperatures given by the makers, those determined by Hoffmann, and the values as corrected by Kanolt. The softening temperatures given in the table correspond to rapid heating.

TABLE I

Cone	Formula of silicate mixture	Softening temperature °C			
		Given by the makers	According to Hoffmann	Corrected for new scale, Kanolt	From corrected and smoothened curve, Kanolt
26	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}7.2\ Al_2O_3\ 72\ SiO_2$	1580	1580	1600	1600
27	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}20.0\ Al_2O_3\ 200\ SiO_2$	1610	1605	1630	1620
28	$Al_2O_3\ 10\ SiO_2$	1630	1610	1635	1635
29	$Al_2O_3\ 8\ SiO_2$	1650	1625	1650	1650
30	$Al_2O_3\ 6\ SiO_2$	1670	1640	1670	1670
31	$Al_2O_3\ 5\ SiO_2$	1690	1640	1670	1685
32	$Al_2O_3\ 4\ SiO_2$	1710	1670	1705	1705
33	$Al_2O_3\ 3\ SiO_2$	1730	1680	1720	1720
34	$Al_2O_3\ 2.5\ SiO_2$	1750	1700	1740	1740
35	$Al_2O_3\ 2\ SiO_2$ [5]	1770	1710	1755	1755
36	$Al_2O_3\ 2\ SiO_2$ [6]	1790	....	....	....

[5] Zettlitz kaolin. [6] Refractory shale, Rackonitz.

Temperatures below cone 26 are not considered, since any clay softening below this point is not regarded as a refractory material.

(c) **Influence of Viscosity.**—As has been said above with reference to the pyrometric cones, the determination of the so-called melting point of clays and other silicates, while important from the industrial standpoint, is in many cases subject to serious variations in the results obtained. Since we are dealing principally with amorphous substances which constantly change in viscosity upon being heated, we can not expect to find any transformation akin to the change of crystalline to isotropic bodies. The softening of such substances to any given degree of viscosity is therefore not only a function of temperature, but of time as well.[7] For

[7] A. V. Bleininger and T. L. Boys: The Time Factor in the Vitrification of a Paving Brick Shale, Trans. Am. Ceramic Soc., 13.

this reason it is possible to vitrify porcelain and other bodies in a short time at a higher and in a longer time at a lower temperature. Partial fusion, sintering, or vitrification may thus go on before any visible evidence of deformation is at hand.

Day and Shepherd found it practically impossible to determine the melting point of quartz-tridymite. As to such minerals as orthoclase and albite, long-continued heating at comparatively low temperatures brings about sintering at temperatures 150° C or more below the melting point, as indicated by the baking together of small fragments and the rounding of edges. In the case of crystals this may take place without loss of crystalline structure.

The factor of viscosity is of as great importance as that of time as regards the deformation and flow of igneous silicates. Great differences exist as to the mobility of different minerals and glasses. While certain silicates, like those of alumina and potash, possess extreme viscosity, others, such as the silicates of lime, soda, and ferrous oxide, are far more fluid and pass rapidly from a state of high viscosity (solid) to one of low viscosity (liquid). The important function of viscosity is thus characterized by Doelter: [8]

> The influence of viscosity is an important one, and it determines all the conditions in silicate fusions; due to viscosity the influence of the medium becomes manifest and consists in retarding the reaction velocity, expressed as velocity of solution, crystallization, fusion, and diffusion. All these values decrease with increase in viscosity.

Vogt [9] likewise has sought to correlate the viscosity of fused magma with the sequence and velocity of crystallization. The work of Tammann [10] especially is of fundamental importance in assembling the facts dealing with the relation between temperature and viscosity.

Greiner,[11] working with an improved Tammann apparatus, showed very interestingly the effect of changes in the chemical composition of silicate mixtures upon the viscosity of melts, using the viscosity of fused Na_2SiO_3 as the standard of comparison.

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[8] Ueber den Einfluss der Viskositæt bei Silikatschmelzen, Zentralbl. f. Min., 1906, p. 193.

[9] J. H. L. Vogt, Die Silikatschmelzen, II.

[10] G. Tammann, Kristallisieren, und Schmelzen, p. 158; Sprechsaal, 1904, p. 35.

[11] E. Greiner, Ueber die Abhängigkeit der Viskosität in Silikatschmelzen von ihrer Zusammensetzung, Inaug. Diss., Jena, 1907.

Thus the increase in the viscosity of the fused mixture with an increase in alumina is well shown in Fig. 5, where curve I represents the molecular composition 1 Al_2O_3 $(SiO_3)_3$, 12 Na_2 SiO_3, and II the melt 1 Al_2O_3 $(SiO_3)_3$, 9 Na_2 SiO_3. The same investigator found that as a rule additions of Al_2O_3 and SiO_2 increase the viscosity and basic constituents reduce it. The bases, however, differ widely among themselves in this respect. Thus, for instance, K_2SiO_3 is far more viscous than the corresponding sodium silicate; FeO brings about a condition of greater fluidity than MgO.

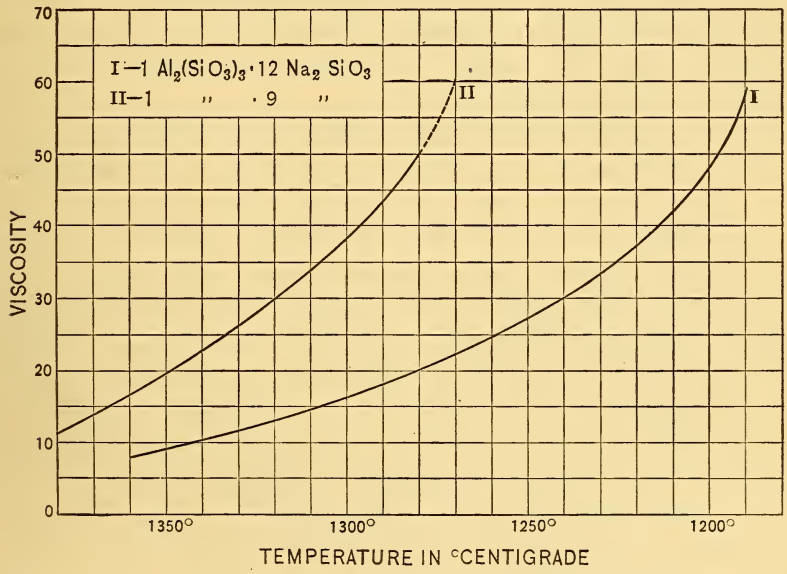

Fig. 5.—*Viscosity curve, showing the effect of alumina upon a soda glass*

According to the acidity of the silicate, CaO may decrease or increase the viscosity, though commonly it may be considered to bring about a more liquid fusion as far as clays are concerned.

With reference to the Seger cones, it is fortunate that up to No. 28 they contain 0.7 equivalent of lime and possess in the series free from lime a constant silica-alumina ratio. The lime is useful in bringing about sufficient fluidity so as to avoid conditions of extreme viscosity, and the constant silica-alumina ratio avoids abnormal fluctuations in the consistency of the melt. However,

as has been pointed out before, the fusion temperatures of even such a well-planned series of compositions can not be determined for the evident reason that such a point does not exist for silicate mixtures of this kind, although we may speak of a softening interval.

This difficulty is especially pronounced in the silicious and aluminous compositions of the higher temperature cones in which the extreme viscosity becomes a critical factor. The saving feature of the Seger cones is the fact that, being of uniform shape and size and being placed in the same position in each test, slanted slightly forward, they are subject to practically the same gravitational pull, and hence bend over as soon as a certain degree of fluidity has been attained.

That the so-called melting point of fire clays is likely to form a deceptive criterion of their refractory value is a common experience. Thus, Purdy [12] found the softening temperatures of evidently inferior clays to be as high as cone 32. The same investigator likewise showed that stoneware clays, vitrifying at comparatively low temperatures and evidently unsuited for refractory purposes possessed softening points of cone 27 and above. Similar results have been found in the clay products laboratory of the Bureau of Standards. This point is also strikingly exemplified in the discordant results obtained in the melting point determinations of several German investigators working with the same materials and mixtures. Thus, while Seger in his kaolin-quartz series found a minimum at the molecular composition 1 Al_2O_3 17 SiO_2, Simonis determined it to be at 1 Al_2O_3, 15 SiO_2, and Flach at 1 Al_2O_3, 12.4 SiO_2.

(d) **Exact Determination of the Melting Point.**—As far as the scientific measurement of the melting point is concerned, it is obvious that the term must be restricted to the fusion of crystalline bodies. The best we can do with amphorous substances is to determine the temperature at some more or less well-defined point of the softening. Thus, Doelter observes the point at which a mineral fragment becomes rounded at the edges, and probably for this kind of work this is as satisfactory as any other method.

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[12] Illinois State Geol. Survey, Bull. No. 4, p. 133.

In the case of anisotropic bodies possessing an ordered, geometrical arrangement of the molecules optical examination becomes the surest guide for the observation of fusion or transformation points.[13] Since fusion, from the exact standpoint, represents a discontinuous change of state which may be located by the discontinuity of some physical property, it may represent the intersection of the vapor tension curves of the crystalline and amorphous states, the point of optical deorientation, the break in electrical conductivity, the discontinuity of the heating curve, the change in the specific volume and other discontinuities. At the same time it must be understood that even the most refined methods of the laboratory will fail in dealing with fusions of great viscosity in which the high internal molecular friction may arrest or greatly delay any changes by means of which the critical point is recognized.

5. EFFECT OF HEAT UPON PURE CLAYS

(a) **Dehydration of Clays.**—Upon heating pure raw clay, corresponding closely to the formula $Al_2O_3 . 2 SiO_2 . 2 H_2O$, under conditions of constant heat supply, as, for instance, in an electric furnace, to increasingly high temperatures, the substance undergoes decided physical and chemical changes. Experiments[14] carried on under the direction of one of the authors in this laboratory, consisting in inserting a thermocouple within clay cylinders 5 cm long and 3 cm in diameter, heating the latter in an electric furnace and plotting the resulting time-temperature graphs showed that two distinct lags occur—one between 200° and 300° C and another completed between 570° and 620° C, according to the kind of clay examined. The beginning of the second lag takes place shortly after 500° C is reached, which thus is the dissociation temperature proper. The first lag evidently is due to the mechanical water held so persistently, the second due to the decomposition of the kaolinite molecule.

With reference to the dehydration of clay, Knote[15] suggests that it breaks up so that two molecules of the clay substance form

[13] Joseph P. Iddings, Igneous Rocks, vol. 1, p. 82.
[14] H. E. Ashley, J. Ind. Eng. Chem., 3, pp. 91–95.
[15] J. M. Knote, Trans. Am. Ceram. Soc., vol. 12; University of Illinois Bull., 7, No. 30.

$Al_2O_3 . SiO_2 + Al_2O_3 . 3 SiO_2$. Mellor [16] proposes the theory that the clay decomposes into free silica, free alumina, and water. The complete proof for either statement is, however, still lacking.

In Fig. 6 the time-temperature graph, as determined from a sample of North Carolina kaolin, is given, in which the end of the dehydration retardation is observed to be 578 degrees.

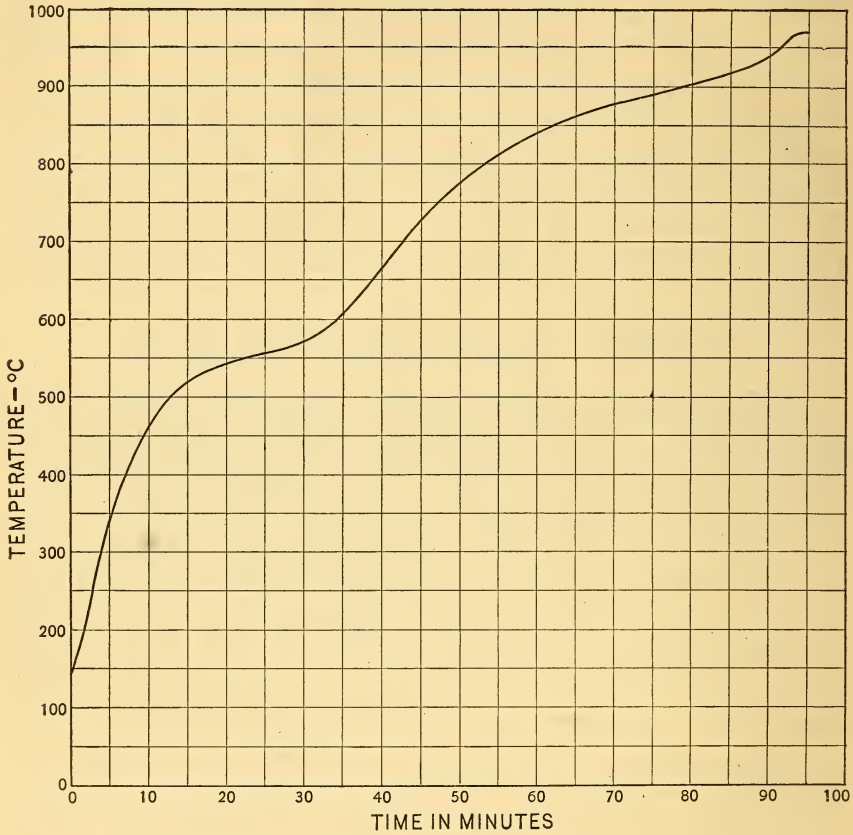

Fig. 6.—*Curve showing the dehydration temperature range of a kaolin*

At about 925 degrees an acceleration takes place, due to some transformation as yet unknown. Knote ascribes it to recombination, resulting in $Al_2O_3 . 2 SiO_2$, Ashley to the possible formation of sillimanite, and Mellor to the polymerization of the alumina. Striking evidence of the deep-seated changes taking place at the

[16] Trans. Eng. Ceram. Soc., **10**, I, p. 114.

dehydration lag and the acceleration point is shown by the work of Knote, who determined the specific gravities of several clays heated to various temperatures. These results are illustrated in Fig. 7, representing the examination of a North Carolina kaolin. It is observed that in spite of the loss of the chemically combined water a drop in the density, i. e., a distinct increase in specific volume occurs. This observation is verified by the experience well known to brick burners and measured with accuracy by Lovejoy.[17] This expansion amounts to about 6 per cent in terms of the original volume. Upon dehydration clays become more readily soluble in acid and alkali solutions, as observed by H. Le Chatelier,[18] F. W. Clarke,[19] Knote,[20] and others. This condition of ready

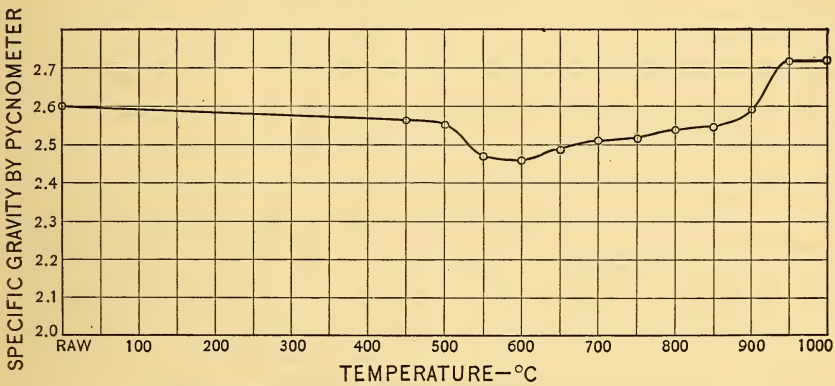

Fig. 7.—*Diagram showing change in density accompanying dehydration*

solubility, characteristic of the amorphous state, disappears as soon as the clay is heated to the point at which the exothermic transformation or reaction occurs. At or just after the dehydration stage the clay substance appears to be in a very receptive condition with reference to chemical reaction. Thus dehydrated clay will combine with calcium hydrate to form a substance possessing the properties of a hydraulic cement, a property which it loses on reaching the chemically inert state.

Le Chatelier has attempted to classify clays on the basis of the observed retardations and accelerations into five types, a procedure which hardly seems justified from the evidence at hand.

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[17] Trans. Am. Ceram. Soc., 7.
[18] Zs. physik. Chemie, 1, p. 396.
[19] U. S. Geol. Survey, Bull., 125, p. 32.
[20] Trans. Am. Ceram. Soc., 12, p. 504.

Clay heated to its dissociation temperature does not necessarily lose its plasticity and may be rehydrated. Purdy [21] found six clays which, after being heated to a sufficiently high temperature, slaked down in water to a plastic mass.

The expulsion of the chemical water, together with the volume increase of the clay mass, leaves the latter in a very porous condition, which in a kaolin may correspond to 30 or more per cent of pore space, in terms of the exterior clay volume. It is evident that the mechanical strength of the material, as measured by its resistance to compression, is very low at this stage.

(b) **Contraction of Clays in Firing.**—As the temperature rises above the dehydration point contraction of the clay takes place analogous to the shrinkage of alumina, magnesia, zircona, and other typically amorphous bodies. This diminution in volume is especially marked in certain very pure clays, and is not of the same nature as the subsequent contraction due to the process of vitrification. The contraction of kaolin begins soon after the chemical water is driven off, when the substance is a typical amorphous body. Lukas,[22] in an investigation of the fire shrinkage of such substances, determined the contraction suffered by small specimens of Zettlitz kaolin. In some clays, as in the case of flint clays, the contraction is especially marked. At somewhat higher temperatures, cone 010 to cone 5, this shrinkage is accelerated by softening due to the presence of basic oxides. Pure clay, however, free from the latter, after passing the contraction in volume conditioned by its physical state, does not shrink appreciably for a considerable temperature interval. This is illustrated in Fig. 1, where with a flint clay contraction practically ceases at cone 05 and then remains quite constant for a long temperature interval, cone 05 to cone 21. The specific volume, entirely aside from the apparent volume of the clay, undergoes changes due to various causes, those brought about by chemical reactions and inversions. A striking example is the condensation in true volume taking place at about 925° C, coincident with the exothermic change noted above.

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[21] Ill. State Geol. Surv. Bull., 9, p. 221.

[22] Zs.f. phys. Chemie, 52, p. 327.

In silicious materials there is found in addition the inversion of quartz to tridymite,[23] which is accompanied by an increase in specific volume, representing a drop in specific gravity from 2.654 to 2.326. There are probably other inversions which are still unknown. The changes in true volume suffered by clays are thus the resultant of the changes experienced by the individual minerals.

(c) **Crystallization of Clays.**—As the temperature rises above 1000° C the effect of any fluxes that may be present becomes more and more evident.

In the absence of basic oxides or of titanium oxide no significant changes seem then to take place until a temperature of approximately 1350° C has been reached. At this stage distinct evidences of crystallization appear, and microscopic examination of thin sections of clay burnt to this temperature reveals the presence of needle-shaped crystals, which have been shown to be sillimanite. Upon separation of this crystalline material from the matrix by means of dilute hydrofluoric acid and subsequent analysis it has been found to be composed of alumina and silica in the molecular ratio of 1 : 1. The mineral, therefore, is sillimanite. Its formation in clays and vitrified clay bodies has been made the subject of investigation by Vernadsky,[24] Glasenapp,[25] Mellor,[26] Plenske,[27] Zoellner,[28] and others.

The conclusion of Glasenapp that "all clays become crystalline at high temperatures coincident with the decomposition of the clay substance" must be taken to have been established. Mellor showed very interestingly the growth of this crystalline structure on refiring and proved that the decrease in the crushing strength of certain refractory products was due in part to this phenomenon. From the work of Zoellner it appears that the formation of sillimanite is not due to crystallization from solution, but to the direct decomposition of the clay substance. The last-named investigator was able to separate from highly refractory clays burnt

[23] A. L. Day and E. S. Shepherd: The Lime-Silica Series of Minerals, Am. Jour. Sci., **22**, p. 265.
[24] Bull. de la Soc. f. de Min., 1890, **13**, p. 256.
[25] Tonindustrie Ztg., 1907, No. 89.
[26] Pottery Gazette, 1907, No. 367.
[27] Dissert., Aachen, 1907.
[28] Sprechsaal, 1908, Nos. 35–39.

to a temperature of cone 15 from 2 to 22 per cent of sillimanite. He also found that the crystallization of this mineral was accelerated by the presence of fluxes and that all hard porcelains contained large amounts of it. In fact, Zoellner suggests the presence of sillimanite as a criterion of a good porcelain.

The mechanical effect of the crystallization of sillimanite upon the clay structure is evidently not negligible, especially with reference to such properties as the coefficient of expansion. The weakening of the clay structure observed by Mellor is perhaps due to the difference between the coefficient of expansion of the crystalline material and the amorphous portions. Owing to the fact that sillimanite is more refractory [29] than the pure clay substance, due to its higher content of alumina, corresponding to a melting point of about 1810° C, it has been suggested that for this reason the ultimate heat-resisting quality of the clay body would be raised by the crystallization of this mineral. It was thought that a crystalline skeleton might be formed which would tend to hold up the clay. This assumption is of course erroneous, owing to the fact that the refractory behavior of the amorphous portion of the body would be correspondingly weakened.

Sillimanite shows no heat effect between 1100° and 1500°. It melts sharply to a very thin liquid which crystallizes with great rapidity even when dropped into water. The density of this mineral (fused preparation) is 3.031, while that of the natural substance is 3.32. Little or no solid solution occurs with sillimanite.

(d) **Final Fusion.**—The final fusion of pure kaolin proceeds gradually, as is typical of the acid alumina silicates, owing to the high viscosity of the mass. The softening temperature of one of the best European kaolins, that from Zettlitz, in Bohemia, as determined by the bending of a test cone, coincides practically with the fusion point of platinum. The Rakonitz shale, another material corresponding quite closely to the typical kaolinite composition but of a denser structure, softens above the platinum melting point, and hence has been taken to represent cone 36. We have thus certain standards of practically pure clay substance which may be used as criteria in determining the refractory values of clays used for commercial purposes.

[29] E. S. Shepherd and G. A. Rankin: The Binary Systems of Alumina with Silica, Lime and Magnesia, Am. J. Sci., 28, pp. 293–334.

6. EFFECT OF THE ACCESSORY CONSTITUENTS OF FIRE CLAYS UPON THE SOFTENING TEMPERATURES

Owing to the fact that clays may contain natural admixtures of various minerals and rock débris, it is necessary to consider the effect of such minerals as quartz, SiO_2; alumina, rutile, TiO_2; ferric oxide and other iron compounds, orthoclose, K_2O, Al_2O_3, $6SiO_2$; muscovite, H_2KAl_3 $(SiO_4)_3$; calcite, $CaCO_3$; magnesite, $MgCO_3$; and other substances. Finally an attempt must be made to estimate the joint fluxing effect of at least the basic oxides with sufficient accuracy for technical purposes.

(a) **Quartz.**—It was realized early in the study of fire clays that any addition of free silica to pure clay substance lowered the softening temperature. Thus, Seger [30] found that a mixture corresponding to the molecular formula, $Al_2O_3 . 17\ SiO_2$, composed of Zettlitz kaolin and ground quartz softened at cone 26, while the clay itself fused at cone 35. This composition represents a minimum point in the fusion curve of the series $Al_2O_3 . 2\ SiO_2$—SiO_2 and hence the eutectic. Expressed in per cent this mixture consists of 90.9 per cent silica and 9.1 per cent alumina, or 23 per cent of hydrous clay substance and 77 per cent of quartz. More recent investigators do not agree with the results of Seger. Simonis found the eutectic formula to be $Al_2O_3 . 15\ SiO_2$, and Flach $Al_2O_3 . 12.4\ SiO_2$. It is possible that both of the latter workers might have employed a sample of kaolin considerably more impure than that used by Seger, a presumption which applies especially to the case of Flach. In part, the discrepancy is due to the difficulty in determining the softening point of the test specimens, as has been pointed out before. Seger's eutectic composition agrees closely with that of Shepherd and Rankin.

The curve of Seger is reproduced in Fig. 8. The softening temperatures of these various mixtures were determined in the Deville furnace. It will be observed that upon the addition of silica the refractoriness of the kaolin is at once decreased at a rapid rate from the melting point of platinum toward the softening point of the eutectic mixture beyond which the curve rises toward the fusion temperature of silica, approximately 1600°.

[30] Hermann A. Seger, Gesammelte Schriften, p. 434.

Silicious clays hence possess an inferior ultimate refractoriness, per se, a fact which must be recognized in the selection of refractories. The addition of quartz also brings about a more or less pronounced increase in volume, which may show itself either by neutralizing the fire shrinkage of the clay portion or by

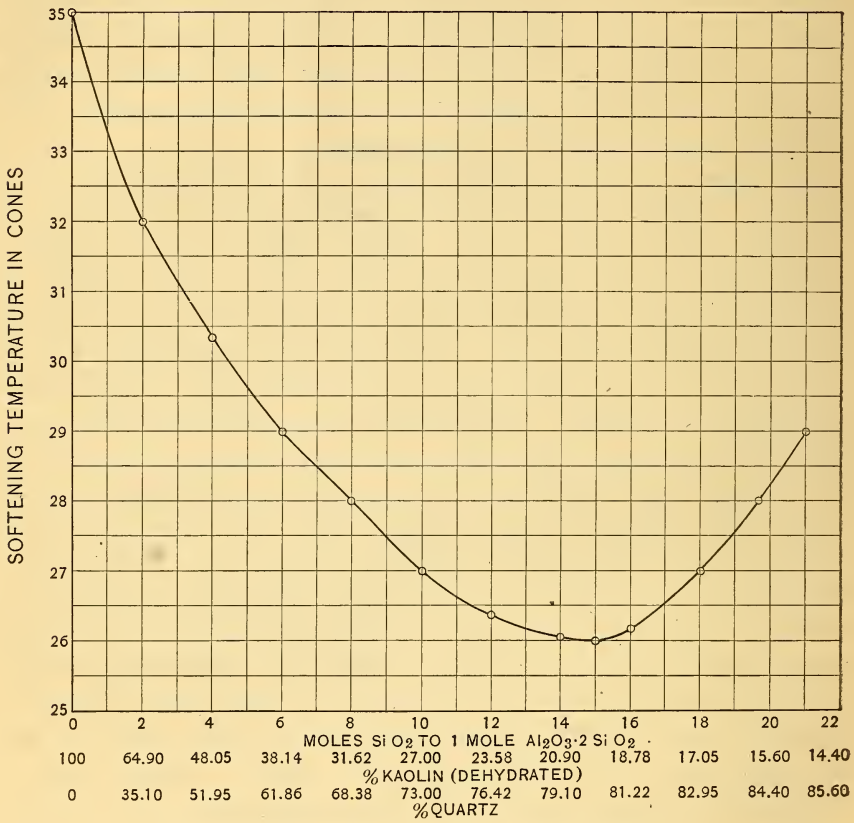

Fig. 8.—*The Seger fusion curve of the system kaolin-quartz*

an actual expansion. This is a fact well known in the industry. The so-called silica brick invariably expand upon being fired in the kiln and usually still further when in actual use. This change is due to the inversion of quartz to tridymite, to which attention has already been called.

Cramer [31] reports results obtained by refiring Dinas bricks five times, in which appreciable expansion is noted, even after the third heating.

(b) **Alumina.**—As a general proposition it may be said that this compound improves the refractoriness of fire clays markedly. Bischof,[32] in his well-known researches upon European fire clays, recognized this fact in his so-called refractory quotient, a value intended to indicate the relative heat-resisting property of these clays expressed by the relation $a^2 \div b$, where a = molecular equivalents of alumina to one molecular equivalent of total fluxes, RO, and b equals the corresponding molecular ratio between the silica and the fluxes. According to this the refractoriness of a clay is proportional to the square of the alumina content. Richters also recognized the value of alumina in this connection. In his experiments additions of alumina raised the softening temperature of kaolin. Upon continuing the increase in alumina the fusion temperature of sillimanite, 1810° C is reached and finally the melting point of alumina, approximately 2000° C. In this part of the silica-alumina series two eutectics [33] are encountered, at about 10 per cent Al_2O_3, 90 per cent $Al_2O_3 . SiO_2$, and at 65 per cent Al_2O_3, 35 per cent $Al_2O_3 . SiO_2$.

The viscosity of silicate fusions is increased most decidedly by additions of alumina, as has been shown by J. H. L. Vogt, Doelter, Greiner, and others. From the practical standpoint the addition of alumina, in the form of bauxite, to fire-clay has been practiced for some years with satisfactory results as far as refractoriness is concerned, but the continued contraction of the bauxite upon reheating makes it a difficult material to work. For high temperature work fused alumina (purified bauxite) is now being introduced where the conditions warrant its use.

(c) **Titanium Oxide.**—This compound, which may be present as rutile, TiO_2, ilmenite, $Fe\ TiO_3$, or in other forms, tends to lower the softening temperature of clays distinctly. This has been shown to be the case by Seger [34] as well as by Rieke.[35] The latter

[31] Handbuch der gesammten Thonwaarenindustrie, p. 896.
[32] Seger's Gesammelte Schriften, p. 435.
[33] Shepherd, Rankin, Wright, and Larsen: Am. J. Sci., 28, No. 166; 1909.
[34] Ges. Schriften, p. 411.
[35] Sprechsaal, 1908, No. 30.

investigator found that an addition of 10 per cent of TiO_2 lowered the softening point from cone 35 to cone 30 and 20 per cent to cone 26. Experiments by Ries,[36] in which he made mixtures of South Carolina clay, possessing a softening temperature of cone +34, with from 0.5 to 5 per cent of TiO_2, showed that 4 per cent of the latter were required to lower the softening point to cone 33 and 5 per cent to bring it down to cone 32.

(d) **Iron Oxide.**—This substance in the finely divided condition is one of the most potent fluxes, and hence its presence in fire clays is very injurious as regards their behavior when subjected to higher temperatures. When present in the form of coarser particles, occurring as siderite or pyrite, its effect is not so marked, since evidently the action is proportional to the surface factor, i. e., the fineness. At the high temperatures to which refractories are exposed the ferric oxide of the clay dissociates to one of its lower forms. According to Le Chatelier[37] this dissociation takes place at 1300°, according to White and Taylor at 1200°, and to P. T. Walden[38] at 1350° C. The last-named value represents probably the most reliable result. At this temperature the dissociation pressure reaches 160 mm, which is equal to the oxygen pressure of the air. Ferric oxide hence can not exist above this temperature. While this limiting temperature corresponds to the reaction

$$3\ Fe_2O_3 \rightleftarrows 2\ Fe_3O_4 + O$$

it does not seem probable that the magnetic oxide would persist at the temperatures involved in contact with a silicate of the fire clay type. The reduction under these conditions very likely results in FeO, which at the temperatures involved would at once combine with silica to form ferrous silicate. This change is hastened by the reducing condition which usually prevails in the atmosphere of fire-brick kilns. Larger lumps of iron oxide embedded in the clay mass may consist in part of ferro-ferric and ferrous oxide, but the finely divided oxide may be assumed to be only FeO. The reaction between the latter and silica progresses exceedingly rapid, and owing to the low fusion temperature of

[36] The Clays and Clay Industry of New Jersey, Vol. VI, p. 71, Geological Survey of New Jersey.
[37] High Temperature Measurements, p. 246.
[38] On the Dissociation Pressures of Ferric Oxide, Jour. Am. Chem. Soc., 30, p. 1350.

the ferrous silicate the resulting slag is very corrosive and attacks the clay vigorously. From the work of Cramer [39] it appears that iron oxide is an active flux with clays of the formula $Al_2O_3 2.5SiO_2$ while it is less active in fire clays approaching more closely the kaolin formula. The addition of 0.2 equivalent $Fe_2O_3 = 0.4FeO$ sufficed to lower the softening temperature of a clay mixture of the formula $Al_2O_3 2.5SiO_2$ from cone 34 to cone 27. Ferrous silicate, $FeSiO_3$, has been estimated [40] to fuse at 1110° C in a reducing atmosphere. However, this value is probably too low. The viscosity of the ferrous silicates is quite low, as has been shown by Greiner, while ferric oxide acts in the opposite direction and increases the viscosity of silicate fusions. The softening temperatures given by Hofman for various ferrous silicates are as follows:

	°C
$4FeO.SiO$	1280
$3FeO.SiO_2$	1220
$2FeO.SiO_2$	1270
$3FeO.2SiO_2$	1140
$4FeO.3SiO_2$	1120

(e) **Alkalies (Feldspar).**—The alkalies present in clays occur predominatingly in the form of feldspar, orthoclase, or albite, although materials of the plastic type may contain adsorbed salts in noticeable amounts. Orthoclase, $K_2O.Al_2O_3.6SiO_2$, in which some of the potash may be replaced by soda, is probably the most common feldspar. The potash feldspar is less fusible than the albite, but neither has a definite melting point. Doelter approximates that of orthoclase to be 1190° and the one for albite at 1120° C. In industrial practice orthoclase is considered to fuse at cone 8, i. e., its viscosity is decreased sufficiently so that it softens and deforms in the prescribed manner.

The feldspars are so-called neutral fluxes, inasmuch as apparently they do not react chemically with the constituents of clay, like lime or magnesia. They seem to play the rôle of a solvent and reduce the refractoriness of a fire clay in a decided manner. Zoellner [41] states that at cone 13 (about 1400° C) feldspar may

[39] Wirkung der Flussmittel in Tonen, Tonind. Ztg., 1895, Nos. 40 and 41.
[40] H. O. Hofman: Trans. Am. Inst. Ming. Eng., 1899, p. 682.
[41] Sprechsaal, 31, p. 535.

dissolve as much as 3.5 per cent of alumina, 14 per cent of clay substance, and 60–70 per cent of fine-grained quartz. The eutectic mixture of orthoclase and quartz consists practically of 75 per cent feldspar and 25 per cent silica. Owing to the decided viscosity of feldspar mixtures their softening point is very uncertain and has no direct connection with the effect upon vitrification. For instance, a porcelain body might become dense and vitreous at a kiln temperature of cone 10 and yet possess a softening temperature of cone 30 or more.

Feldspar has a more marked effect upon silicious clays or bodies than upon clay substance. Even a kaolin-feldspar mixture high in the latter shows a high softening point. This is illustrated by the work of Simonis,[42] who found that an addition of 15 per cent of orthoclase to Zettlitz kaolin (softening temperature cone 35) reduced this point only to cone 33–34, while one of 30 per cent lowered it to cone +31, and one of 45 per cent to cone 28.

Thus, owing to the high viscosity of feldspar its mechanical softening effect is not as marked as it would be if an equivalent amount of free alkali were added. The presence of feldspar, therefore, in fire clays, while depressing the softening point, is not as detrimental to the refractory quality of the material as might appear at first. Its influence, however, upon the load-carrying ability is far more marked, since the solution effect is great enough to reduce the viscosity sufficiently to prevent the body from carrying heavier loads, though not enough to cause deformation under its own weight.

(f) **Mica.**—This mineral, represented principally by muscovite, $H_2KAl_3(SiO_4)_3$, while depressing the softening point of a pure clay, behaves as a less effective flux than orthoclase, due both to its composition and to its physical structure. It required 20 per cent of mica to lower the softening temperature of Zettlitz kaolin from cone 35 to cone +34, 30 per cent to bring it down to cone +33, and 40 per cent to cone 32.[43]

(g) **Lime.**—The potency of lime as a fluxing agent in acid silicates is well known. Cramer[44] found that additions of calcium carbonate, from 0 to 10 per cent, to Zettlitz kaolin lowered the softening temperatures of the resulting mixtures steadily, practi-

[42] Sprechsaal, 1907, Nos. 29 and 30. [43] Rieke, Sprechsaal, 1908, No. 42. [44] Tonindustrie Ztg., 1887, p. 197.

cally in proportion to the increase in the lime content. Rieke [45] determined the softening temperatures of mixtures, consisting of finely ground kaolin and marble in different proportions. He obtained the following values:

TABLE II

Content of $CaCO_3$ in raw mixture, in percentage	0	1	3	5	6	7.2	8.8
Softening temperature, in cones	+35	35	+33	33	−33	−32	30–31
Content of $CaCO_3$ in raw mixture, in percentage	10	20	30	40	50	60	80
Softening temperature, in cones	−30	15	−15	+8	7–8	16	23–24

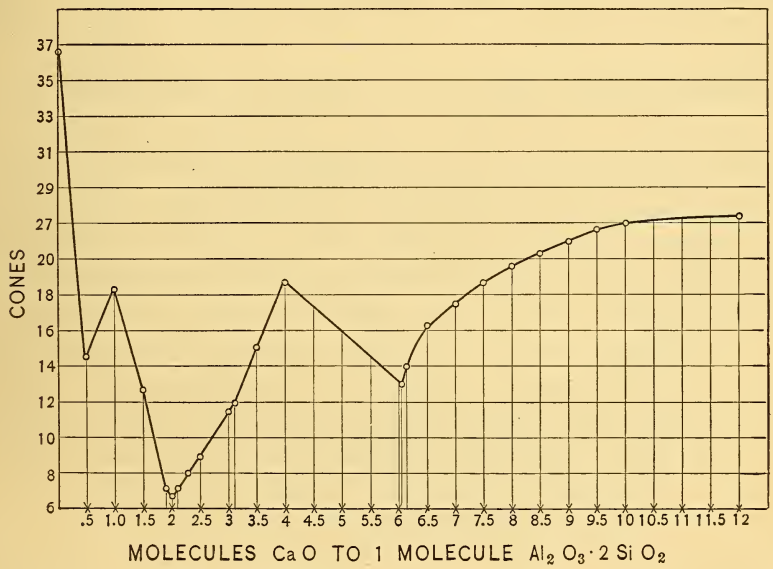

Fig. 9.—*Fusion curve of the system kaolin-lime*

Rieke found that the observation of Cramer, mentioned above, held in that additions of lime to kaolin decrease the softening temperature according to a linear relation up to a mixture containing 11 per cent CaO in the calcined condition, corresponding to the formula $CaO.2Al_2O_3.4SiO_2$. Beyond this point lime no longer reacts in a continuous manner, but shows maxima and minima, indicating the existence of a least two compounds, as

[45] Sprechsaal, 1906, Nos. 37 and 38.

shown on Fig. 9. With more silicious clays the conditions are more complex, resulting in four maxima with a clay corresponding to $Al_2O_3 . 3SiO_2$, Fig. 10.

Since in the discussion of refractories the large percentages of lime are only of secondary interest, a detailed analysis of these fusion curves is not of importance. For the present purpose the simple relation of the lime content up to 11 per cent suffices to indicate the fluxing effect of this base.

The viscosity of the calcium silicates of the more acid type is quite low, as is shown by practical experience in the working of

Fig. 10.—*Fusion curve of the system $Al_2O_3 . 3SiO_2$-lime*

calcareous clays. It is a well-known fact that such materials deform and flow when heated in the kiln beyond the vitrification temperature more readily than other clays. However, this observation does not hold for glasses, as Greiner has shown that in soda-lime glasses the lime invariably raises the viscosity of the melt.

(h) **Magnesia.**—The fluxing effect of this oxide upon pure clay having a softening temperature of cone +35 is illustrated by the results of Rieke,[46] given in the following table:

[46] Sprechsaal, 1907, No. 17.

TABLE III

Per cent of $MgCO_3$	1	3	5	10	15
Softening temperature, in cones	+34	33	−32	−29	−27
Per cent of $MgCO_3$	20	25	30	35	40
Softening temperature, in cones	+16	15	13	11	10

The most fusible mixture consists of 40 per cent of $MgCO_3$ and 60 per cent of hydrous kaolin. Down to about 15 per cent of magnesium carbonate the softening temperature is lowered practically according to a linear relation. Magnesia lowers the viscosity of acid silicate mixtures in a less marked manner than ferrous oxide.

7. JOINT EFFECT OF FLUXES UPON THE REFRACTORINESS

(a) **Richters' Law.**—Many attempts have been made to correlate the effect of the basic fluxes upon the softening temperature of fire clays. Thus Richters [47] in 1868 enunciated the rule that molecularly equivalent amounts of the bases exert the same effect in depressing the softening temperature of fire clays. According to this rule, 40 parts, by weight, of magnesia, would lower the refractoriness to the same extent as 56 parts of lime or 94 of potash. This statement is supposed to apply only to small amounts of these substances added to the purer type of clays. Richters thus gives a rule which 20 years later appeared as the well-known law governing the lowering of the freezing point of aqueous solutions. Cramer [48] repeated the work of Richters' and practically confirmed his results. The action of the fluxes as found to apply by Cramer is represented in the diagram of Fig. 11, illustrating the effect of equivalent amounts of oxides upon Zettlitz kaolin.

The effect of the fluxes upon more silicious clays was found to be much more marked. Ludwig [49] considered Richters' rule a special case of the general law of dilute solutions, or Raoult's law. He restricted its application to very dilute solutions, i. e., pure

[47] Inaug. Diss. Reprint, 2d ed., Tonindustrie Ztg., p. 1897.
[48] Tonindustrie Ztg., 1895, pp. 633 and 647.
[49] Tonindustrie Ztg., 28, p. 773.

clays containing a small amount of fluxes, assuming intimate mixture and considering the iron oxide to be present as FeO. Upon this basis he estimated the softening temperature from the chemical analysis by expressing the composition in the form of an empirical chemical formula in which all of the fluxes, K_2O, Na_2O, CaO, MgO, and FeO, are combined in one expression as RO, while the alumina is made constant and equal to unity. This gives two variables, RO and SiO_2. From the analysis and the determina-

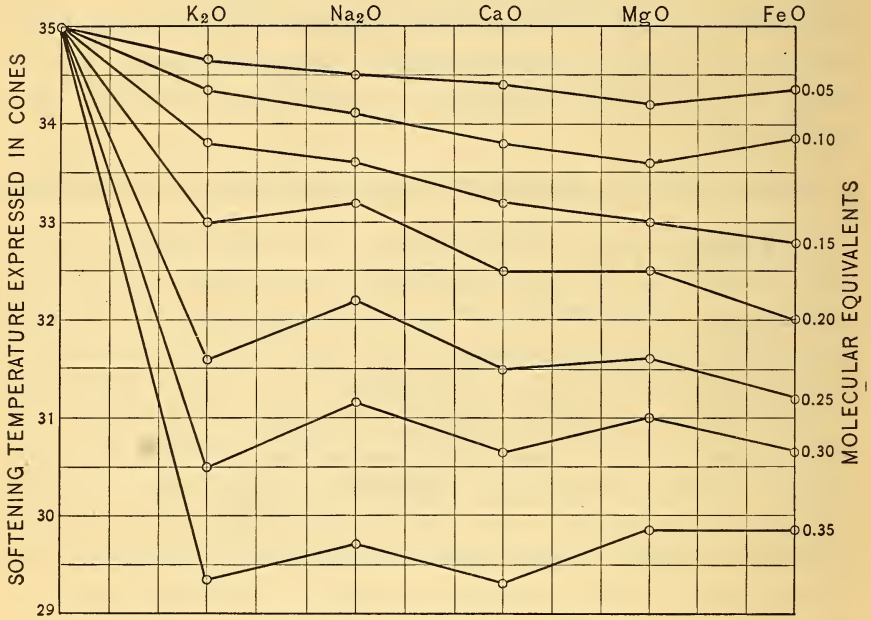

Fig. 11.—*Cramer's diagram showing the influence of equivalent amounts of fluxes upon the softening temperature*

tion of the softening temperature of a number of German fire clays Ludwig compiled a plot with the above variables and showing temperature areas by means of isothermal lines. This chart is reproduced in Fig. 12.

Richters' rule was not questioned, except when attempts were made to consider it as a special case of Raoult's law, until 1910, when Rieke [50] went over the same ground. In this work it was

[50] Sprechsaal, 43, pp. 198–200, 314–317, 229–232.

shown that the effect of equimolecular amounts of the various basic oxides is not the same as regards the lowering of the softening temperature and attention is called to the fact that this is shown to be the case even in Cramer's curves. In the alkaline earth group it was found that the oxides of lowest molecular weight lower the softening point most markedly and those of higher molecular weight least, considering equivalent additions. An analogous regularity exists in the alkali group. Similar results have been obtained by Flach.[51] This worker found the most

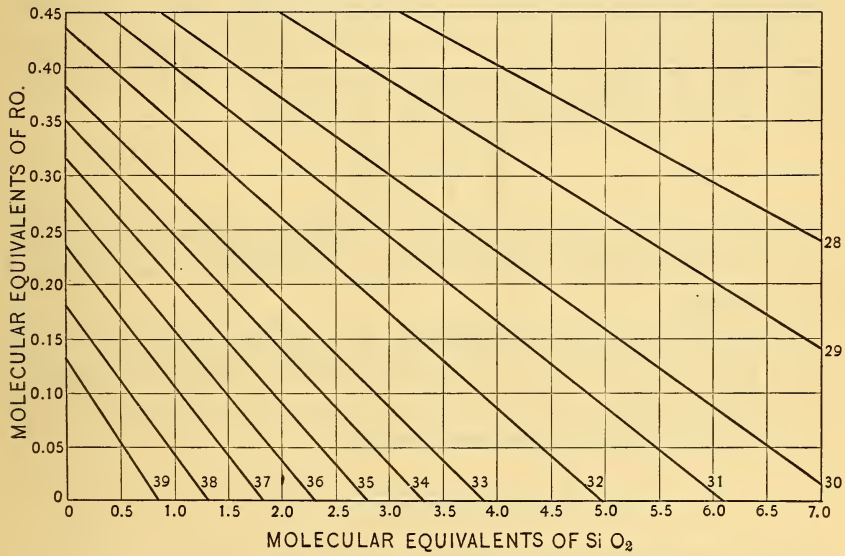

Fig. 12.—*Ludwig's diagram showing the relation between the RO-SiO_2 content of German fire clays and their softening temperatures. The numbers between the iso-therms indicate cones*

fusible SiO_2–Al_2O_3 mixture to be that represented by the formula 1 Al_2O_3 12.4 SiO_2. He says: "The law of Richters, as well as the so-called fusibility factors, do not hold for mixtures carrying more fluxes than the natural clays. The displacement of the eutectic takes place toward that side of the mixtures which shows an excess of Al_2O_3 as compared with the eutectic of SiO_2 and Al_2O_3 (1 Al_2O_3 12.4 SiO_2). Lithium is an exception which with a 10 per cent addition moves the eutectic to the quartz side. In most cases

[51] Sprechsaal, 44, pp. 171–173, 187–189, 205–207, 219–221.

equal lowering of the fusion point brings about equal displacement of the eutectic." The carbonates of the alkaline earths lower the fusion temperatures the more the lower the silica content becomes until the minimum melting point is reached. Magnesia, which Richter and Bischof considered to possess the greatest fluxing power, proved to be a less potent flux than the oxides of calcium, iron, cobalt, and nickel.

(b) **Bischof's Refractory Quotient.**—Bischof [52] proposed a so-called refractory quotient calculated from the formula obtained from the chemical analysis. Letting the molecular equivalents of $Al_2O_3 = a$, those of the $SiO_2 = b$, and of the fluxing oxide $= c$, and expressing the ratio $a \div c$ by A and the ratio $b \div a$ by B, the refractory quotient is represented by the expression

$$\frac{A}{B} = \frac{a \div c}{b \div a} = \frac{a^2}{bc}.$$

According to this the refractoriness would be proportional to the square of the alumina and inversely proportional to the silica and flux contents.

Expressed somewhat differently by making the sum of the fluxes (RO) equal to unity (on the molecular basis) the composition would be represented by the formula 1 RO a Al_2O_3 b SiO_2 and the Bischof refractory quotient becomes:

$$a \div \frac{b}{a} = \frac{a^2}{b}.$$

This expression has been criticized by Seger, Hecht, and others on the ground that the quotient does not agree with the facts, since it has not been demonstrated that the refractoriness increases as the square of the alumina content. Seger suggested a modification of the quotient, but at the same time realized that such a formula could have but little value, owing to the various factors which enter into the question of refractoriness and which do not find expression in the above relation.

(c) **Effect of the RO in the Seger Cone Series.**—The effect of a combination of fluxing bases, composed of 0.3 equivalent K_2O and 0.7 of CaO, upon a silicious mixture of the formula

[52] Die Feuerfesten Tone, 2d ed., 1895, p. 67.

1 Al_2O_3 10 SiO_2 is illustrated by the Seger cone series. The relation between varying equivalents of fluxes and the softening temperature is shown in Fig. 13, where curve A refers to the cone numbers and B to the temperatures as determined by the Reichsanstalt and used by the Tonindustrie Zeitung Laboratory in their last list of softening temperatures. It is interesting to note in this connection a break in the curve between numbers 21 and 27, since

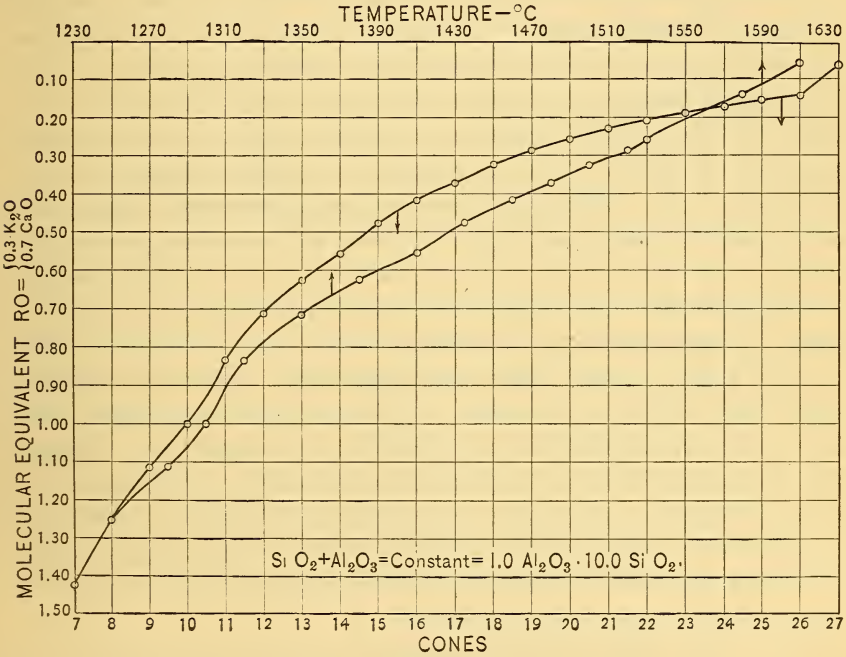

Fig. 13.—*Diagram illustrating effect of RO content in Seger cone series. One curve refers simply to cone numbers, the other to the softening temperatures, as observed by recent investigators*

it has been found by actual determination that the softening points for cones 21–26 showed very close intervals, not in accord with the presumed step of 20 degrees between two numbers.

(d) **Vitrification.**—Vitrification as related to refractory behavior of clays.

It is agreed by workers in this field that the fluxes bring about a large part of the contraction suffered by clays upon being heated to elevated temperatures. While the action due to this cause, as

measured by the contraction in volume, is but slight at lower temperatures, it is accelerated as the temperature rises. This is due to the fact that solution is in progress. Starting from the initial temperature of activity such a selective solution of the fluxes, alumina and silica, tends to take place which softens at this point. With the rise in temperature the composition of this softened portion changes by the incorporation and solution of more of the clay body, and evidently the mass of the softened portion increases correspondingly. Thus with every advance in temperature the softened portion constitutes a larger percentage of the whole, until finally it possesses the composition of the body, i. e., when all of it softens and the so-called melting point has been reached. With the growth in volume of the softened portion, contraction (fire shrinkage) goes on simultaneously. The initial pore space is being filled in by the flow of the softened material. However, the rate of this contraction is not merely proportional to the temperature, but is also a function of the viscosity at any given point. If at any stage the viscosity has been lowered the contraction will take place more rapidly per unit temperature increase than when the mass possesses a higher degree of molecular cohesion. Thus it has been found [53] that with some porcelains the rate of contraction was more marked between cones 4 and 5 than at any lower or higher temperatures. It is assumed that the viscosity of the softened portion was lower during this interval and hence under the inward pressure of the surface forces at work the resulting flow into the poral spaces was increased.

As to the cause of this contraction it may be said to be that force which, in the case of liquids, produces drops and which will cause the fluid to assume the smallest possible surface area. J. W. Mellor [54] gives the following concise definition of the softening temperature: "The softening temperature measures the temperature at which the inward surface pressure of the substance becomes greater than those intermolecular forces which hinder the molecules taking up a position of stable equilibrium-minimum surface area."

[53] A. V. Bleininger and R. T. Stull: Trans. Am. Ceramic Soc., **12**, pp. 629–675.

[54] J. W. Mellor, A. Latimer, and A. D. Holdcroft: The Softening Temperatures of Lead-Silica Glasses, Trans. Eng. Ceram. Soc., **9**, pp. 126–149.

(e) **Decrease in Density During Vitrification.**—It is interesting to note also that during the solution process going on throughout vitrification the density of the clay mass itself decreases proportionally to the contraction in pore space. In other words, the vitrification and fusion of clays causes them, in common with most silicates, to increase in volume. Thus, although a piece of clay ware shrinks in exterior volume in burning, its real volume increases. To illustrate, the well-known flint clay from Mount Savage, Md., which in a raw state has a density of 2.60, shows at cone 23 a density of 2.53, corresponding to an increase of 2.7 per cent in volume. The higher the clay is in impurities the lower is the temperature at which this drop in specific gravity becomes manifest. A high-grade plastic clay from Olive Hill, Ky., possessing a density of practically 2.60 in the raw state, had a specific gravity of 2.38 at cone 23, equivalent to a growth in true volume of 8.46 per cent.

From what has been said it is apparent that the more fluxes a clay contains—i. e., the more deficient in refractoriness it is—the lower must be the temperature at which all pore space has been filled by the softened matter; in other words, the lower its temperature of vitrification. Hence by obtaining a plot correlating burning temperature with shrinkage or porosity we should have a very clear picture of its refractory behavior. This indeed is the case and determinations of this kind are infinitely more valuable than theoretical considerations based merely upon chemical analysis.

(f) **Measurement of the Rate of Vitrification.**—The following criteria may be employed in measuring the rate of contraction: (1) Linear measurement of shrinkage; (2) volume measurement; (3) measurement of water absorption; (4) measurement of porosity.

The linear contraction is obviously measured by means of rules, calipers, or micrometers, according to the degree of accuracy desired.

The measurement of the contraction in volume is much more accurate than linear measurements and is accomplished by completely saturating the test specimen in water and obtaining the volume direct by means of the Seger or similar voluminometers.

Where the initial volume of the unburnt, dry specimens is desired, the measuring fluid should be preferably xylol, or heavy kerosene may be used, thoroughly freed from the lighter hydrocarbons by heating.

The porosity is usually expressed in per cent of the initial exterior volume.

The measurement of water absorption is an indirect means of gauging the porosity and is not desirable from the standpoint of accuracy. For this purpose the specimens are either partially immersed in a covered vessel under atmospheric pressure or placed under water in tight receptacles in vacuo. The absorption is usually expressed in terms of the dry weight.

The porosity is determined by weighing the dry specimen, saturating with water by boiling in vacuo and obtaining the weight of the saturated piece as well as its weight when suspended in water. By means of the simple obvious relation

$$P = \frac{100\,(W - D)}{W - S}$$

where P = per cent porosity
W = wet weight of specimen
D = dry weight of specimen
S = weight of specimen suspended in water

the porosity of the clay in question may be calculated. Owing to the fact that this method depends solely on weighing operations, it is carried out most readily. For laboratory work it is desirable that for this purpose the specimens be not too large. Test pieces weighing, dry, from 30 to 50 grams permit of rapid working.

For investigation purposes, where a definite basis of comparison is essential, it is advisable to refer shrinkage and porosity to the true volume of the clay, i. e., weight ÷ density, where the latter is the specific gravity of the powdered material.

In Fig. 14 the porosity-temperature curves of eight well-known flint and plastic fire clays are given, which show at once the rate at which vitrification progresses. In all this work the cone softening points are used as the expression for temperature, inasmuch as to a certain extent these take into account the very important time element.

(g) **Effect of Time.**—It is a well-known fact, to which attention has been called before that the rate of heating has an important influence upon the changes that are produced—in this case the closing up of the pore space. In order to reduce the porosity to a given point, a higher temperature must be attained if the rate of heating is rapid than when it is slow.

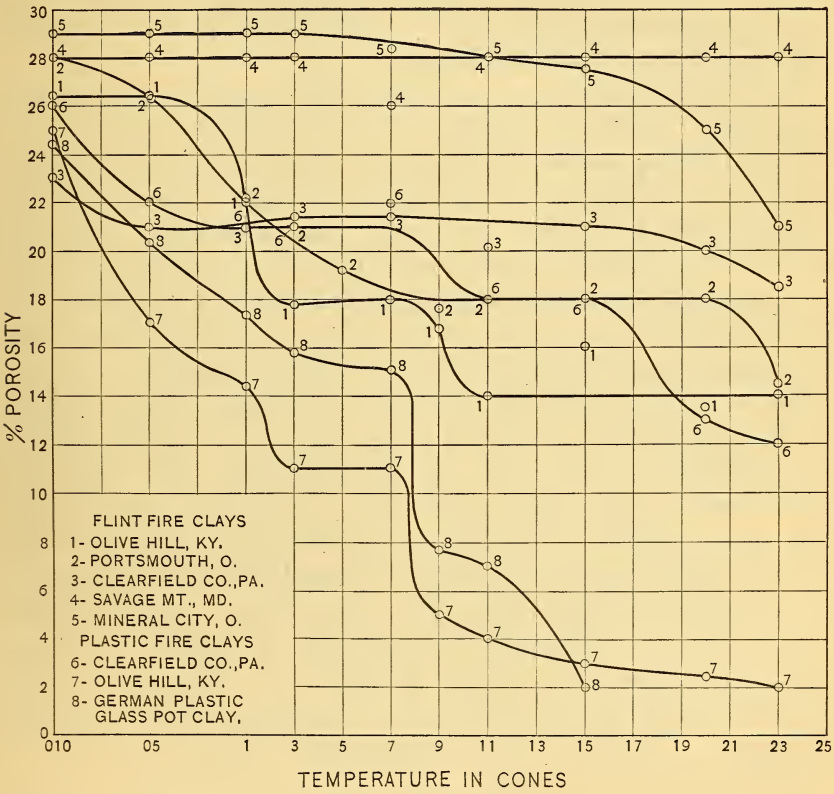

Fig. 14.—*Porosity-temperature relations of eight fire clays*

Thus Bleininger and Boys have shown that in the case of a shale a certain porosity, 10 per cent, was reached after heating for 72 minutes at a constant rate from atmospheric temperature to 1200° and likewise in 536 minutes at the temperature of 1150° C. The rates of heating were 16.6 degrees and 2.1 degrees per minute, respectively. All other conditions were maintained uniform.

Hence the cone softening points are to be preferred for this kind of work, since their fusion represents a heat effect similar to that being performed within the clay. It is important, however, to realize that the rate of heating must not be too rapid. For this reason ceramists now employ test kilns of as large size as possible, so that the rate of heating is necessarily slow and as a rule does not exceed 5 degrees per minute, assuming that test specimens of laboratory size are being burned. Softening-point determinations may be fired at a more rapid rate.

It must be realized that in burning clay products conditions of equilibrium are never reached. The contraction resulting at a certain finishing temperature is by no means constant, and upon reheating the product to the same temperature an additional shrinkage will be noted. The higher the temperature, however, the less will be the contraction upon reburning, a point which has an exceedingly important bearing upon the use of refractory clay ware. Whatever may be the use for which the material is employed, the burning temperature should be as high as possible.

Mellor,[55] in discussing the speed of vitrification of clays, analyzes the data obtained in reburning bone china, and calls attention to the similarity between the rate of contraction with successive firings and the law for the velocity of a bimolecular chemical reaction, which involves, of course, the assumption "that the change of contraction during each firing is proportional to the square of the contraction which has yet to take place." Mellor further makes use of the calculation in question, in which x = observed contraction after any number of firings, t. Hence $a-x$ represents the contraction which is yet to take place after any number of firings, t. Then the rate of contraction is given by

$$\frac{dx}{dt} = K(a-x)^2.$$

Integrating, the expression becomes

$$K = \frac{1}{t}\int \frac{dx}{(a-x)^2} = \frac{x}{at\,(a-x)}.$$

This interesting analogy thus presented by Mellor is, of course, a

[55] Trans. Eng. Ceram. Soc., 9, pp. 79–92.

coincidence, though he has succeeded in showing a very striking agreement with this assumption and one set of experimental results.

8. TESTING OF CLAYS FOR GENERAL REFRACTORY PURPOSES

(a) **General Considerations.**—In determining the value of a fire clay it is obvious from what has been said before that it is important to consider the purpose for which it is to be used. Thus it would be absurd to require high refractoriness for clays to be made into bricks which are to go into the top of a blast furnace lining where resistance to abrasion at a low temperature is the consideration. In other words, we must clearly recognize the conditions to be met. It also is evident that plastic bond clays can not in the nature of the case be expected to come up to the refractoriness required of the flint clays, which constitute the bulk of the mixtures.

In this work, however, the discussion will be confined mainly to the question of refractoriness, which constitutes, after all, the principal demand made of fire-clay products. Other desirable physical properties may often be obtained by proper treatment in the manufacturing process, such as the correct proportioning of flint, plastic fire clay, and grog, with reference to sizing and intimacy of mixture, and especially the degree of firing.

(b) **Testing Methods.**—The testing methods available for the examination of fire clays are the direct determination of the softening temperature, of the temperature-porosity relation, and chemical analysis. In attempting to put down specific requirements to be met by fire clays at least two classes must be distinguished—No. 1 fire clays of high refractoriness and No. 2 clays of somewhat inferior refractoriness, but necessary as bonding material. While it would be highly desirable that the No. 1 clays be as plastic as possible, the requirement as to plasticity becomes an urgent one in the case of the No. 2 fire clays, since without well-developed bonding quality the latter becomes practically valueless.

With reference to the No. 1 clays an arbitrary minimum refractoriness must be assumed.

From the numerous tests made by the writers with American materials it seems that this limit for the softening temperature

should be put at cone 32. In testing a clay of this type in the Deville or in an electrical furnace in comparison with standardized Seger cones its degree of softening should correspond to the No. 32 cone.

(c) **Classification of Fire Clays.**—As to the classification of No. 1, fire clays with reference to their temperature-porosity curves the results given in the diagram of Fig. 14 will permit of a fair comparison. Attention must be called in this connection to the fact that the porosities in themselves are not of special significance, but that the rate of porosity decrease is of primary importance. Purdy [56] was first to make the rate curve the basis of classification and has worked out a porosity diagram (Fig. 15) for No. 1, No. 2, and No. 3 fire clays to a temperature of cone 11, a temperature which is, however, not high enough for this purpose. The upper limit for No. 1 fire clays given by him does not agree with the porosity curves of a number of well-known clays, especially those of the flint type. Likewise, his lower limit is too high for many excellent plastic refractory clays. However, his method of arriving at a basis of comparison for the grading of the various fire clays is thoroughly sound. At the present time the number of clays examined is too small for the definite statement of permissible limits.

(d) **Limits of RO Constituents.**—As regards the chemical composition of fire clays attention has already been called to the effect of the various constituents of clays. Thus Seger's curve and the diagrams of Cramer and Ludwig point out the function of silica and the fluxes and show that the composition: $Al_2O_3 . 2 SiO_2$ is most to be desired from the sole standpoint of refractoriness. The effect of the total basic fluxes, RO, it has been seen, becomes very prominent at about 0.2 molecular equivalent as expressed in the empirical formula commonly employed in ceramic studies. In these formulæ alumina is made equal to unity. To calculate it from the results of the chemical analysis divide the per cent of each component by its molecular weight. Add the equivalents of K_2O, Na_2O, CaO, MgO, and FeO thus obtained. Divide the alumina equivalent into the total RO and the SiO_2 equivalents. The result is an expression of the type x RO 1 Al_2O_3 y SiO_2, in which the value of x should not exceed 0.2 for a No. 1 fire clay.

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[56] Ill. State Geol. Surv., Bull., 9, p. 221.

There is of course no sharp distinction between the No. 1 and the No. 2 fire clays and any lower limits that may be set must be, in the nature of the case, arbitrary. From a detailed study of the firing behavior of stoneware and other plastic clays, it seems to the writers that cone No. 28 might be considered the limit below which a satisfactory bond clay should not soften. Clays possessing a lower softening point may, of course, be used to bond high-grade flint clay, but the result, in spite of the fact that the high-grade clay is far in the excess of the low-grade material, does not make for high

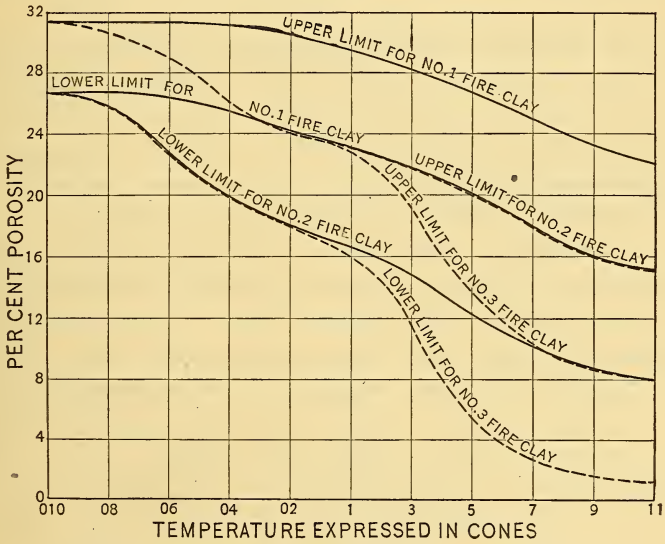

Fig. 15.—*The classification diagram for fire clays by Purdy*

quality. In many cases it would be advisable to improve the standing-up quality of the bond clay by intimate grinding and admixture with flint clay.

With reference to the temperature-porosity curve of the No. 2 fire clays no definite limits can be set at present. The limiting curve suggested by Purdy is probably the best attempt to define this boundary.

As to the chemical composition it might be said that 0.3 equivalent RO should in no case be exceeded.

9. EFFECT OF HEAT UPON THE LOAD-CARRYING CAPACITY OF REFRACTORIES

(a) **Use of Load Conditions as a Means of Measuring Viscosity.**—In the preceding paragraphs the fact has been established that clays do not possess a melting point, but that they gradually soften until deformation takes place. The viscosity is diminished at the same time from that possessed by the solid body to the degree of fluidity shown by the fused mass. It thus becomes simply a question as to which stage of the decrease in viscosity we consider the softening point.

For all practical purposes a fire brick is completely distorted at temperatures considerably below that at which it "goes down" when tested in the laboratory furnace. Thus the knowledge that a certain material softens completely at a given temperature does not tell us when its viscosity has been decreased to such a degree that it is unable to stand up under furnace conditions.

Hence in order to overcome the viscosity effect it evidently seems desirable to bring about testing conditions which give expression to the practical failing point. This is accomplished by the application of a load upon the specimen under test. This load, however, should have some relation to the requirements of practice. It should not be so large as to tax even the compressive strength of the specimen in the cold condition, as was done by Haag, who employed a load of about 500 pounds per square inch, nor should it be smaller than the maximum loads required of refractories in actual use. The loads should be somewhat greater than the maximum furnace loads, since obviously the time element, which is such an important factor under actual conditions, can not be reproduced in the laboratory. To be useful at all the time of the test must be short enough to enable it to be carried out without too much delay.

Tests have been made upon the compressive strength of fire brick specimens at 1000° C by Gary,[57] who found that at this temperature the material showed greater strength than at atmospheric temperatures. In one case the crushing strength, cold, was 169 kg, while at 1000° it rose to 218 kg per sq cm. This work, the account of which was published after the present investigation was com-

[57] Mitt. Kgl. Materialprüfungsamt, 28, pp. 23–40.

pleted, shows clearly that at this temperature no lowering of the viscosity is to be observed.

From the work of Heraeus [58] we have some knowledge of the viscosity and the softening temperatures of some standard German fire clays. In the work being quoted the temperatures at which an iridium rod, 9 sq mm in cross section and exerting a pressure of 400 grams per sq mm, began to sink into the softened clay, as well as that at which the penetration speed of 1 mm per minute was reached, were determined with accuracy.

In the following tabulation the values referring to the load mentioned, equivalent to about 550 pounds per square inch, are given in degrees centigrade:

TABLE IV

Clay	Beginning of penetration	Speed of penetration of 1 mm per min. reached at—	Softening temperature (melting point)
Rackonitz shale	1475	1710	1760
Clay No. 6, Gruenstadt	1400	1570	1725
Saarau kaolin	1320	1700	1750
Kaehrlich clay	1450	1510	1670
Palatina clay, Gruenstadt	1420	1670	1725
Clay Qu 7, Gruenstadt	1450	1590	1740
Clay Qu A, Gruenstadt	1410	1500	1670

Since in standardizing the thermocouple the melting point of platinum was taken to be 1780°, these temperatures are somewhat high and should be corrected accordingly.

In the present work it was decided to work with moderate loads and at average furnace temperatures. For this purpose a number of experiments were carried out with loads varying from 175 pounds to 25 pounds per square inch. Likewise preliminary tests were made as to the best temperature, it being desired to adopt that point at which distinct evidence of softening occurs. The work of Lemon Parker and Otto Hensel [59] was also consulted. After considerable preliminary experimentation it was decided to carry on two series of tests, one at 1300° C and a load of 75 pounds per square inch and another at 1350° C and 50 pounds per square inch.

[58] Z. f. angew. Chem., 18 (1905), 49.

[59] Trans. Am. Ceram. Soc., 7, pt. 2.

(b) **Testing Furnace.**—It was also decided to use full-size bricks. This made necessary the construction of a furnace, illustrated in Fig. 16, with an interior space of 20 by 20 by 21 inches, heated by means of eight Fletcher burners, which were supplied with natural gas and compressed air. The combustion gases escape through holes along the back side of the furnace. The back wall consists of a movable door made from a heavy wrought-iron frame, lined with fire bricks. The frame is hung from two rollers, running on an overhead track, so that it can be easily moved. The brick to be tested is firmly placed on end upon a heavy fire-clay block about 9 inches from the door and fixed in position by means of fire-clay mortar. Half of a chrome brick is then placed upon the test specimen, and on top of it a long cylinder made from high-grade fire clay which extends through a hole in the arch of the furnace. The load is then applied upon a cast-iron knife-edge plate by means of a steel I beam 9 feet long, with a distance of 3 feet between the pin taking the upthrust and the fulcrum and 6 feet between the latter and the point of load application. The weight of the beam is 155 pounds. The weight applied consists of a wooden box containing the necessary weight of shot. The beam was first calibrated by means of a platform scale. The pin at the end of the beam passes through a cast-iron block sliding in a channel iron provided with a slit and a heavy fastening bolt. Two bolts are arranged on top of the block so that it can be lowered by loosening the fastening bolt and tightening the top nuts. In this manner the I beam may be kept level throughout the test, thus avoiding side strains upon the brick.

Through an opening in the door a thermocouple is inserted, which is placed as close to the brick as possible.

(c) **Rate of Heating.**—The first point it was necessary to determine was the rate at which a fire brick could be heated up and the time required until the interior of the test specimen had assumed the temperature of the furnace. For this purpose a fire brick was taken and a hole drilled to the center of the brick. A thermocouple was then inserted and the hole well plugged up, leaving the couple covered for some distance away from the brick. Another couple was placed close to the brick, but not touching it. The outside junctions of both thermocouples were placed in test

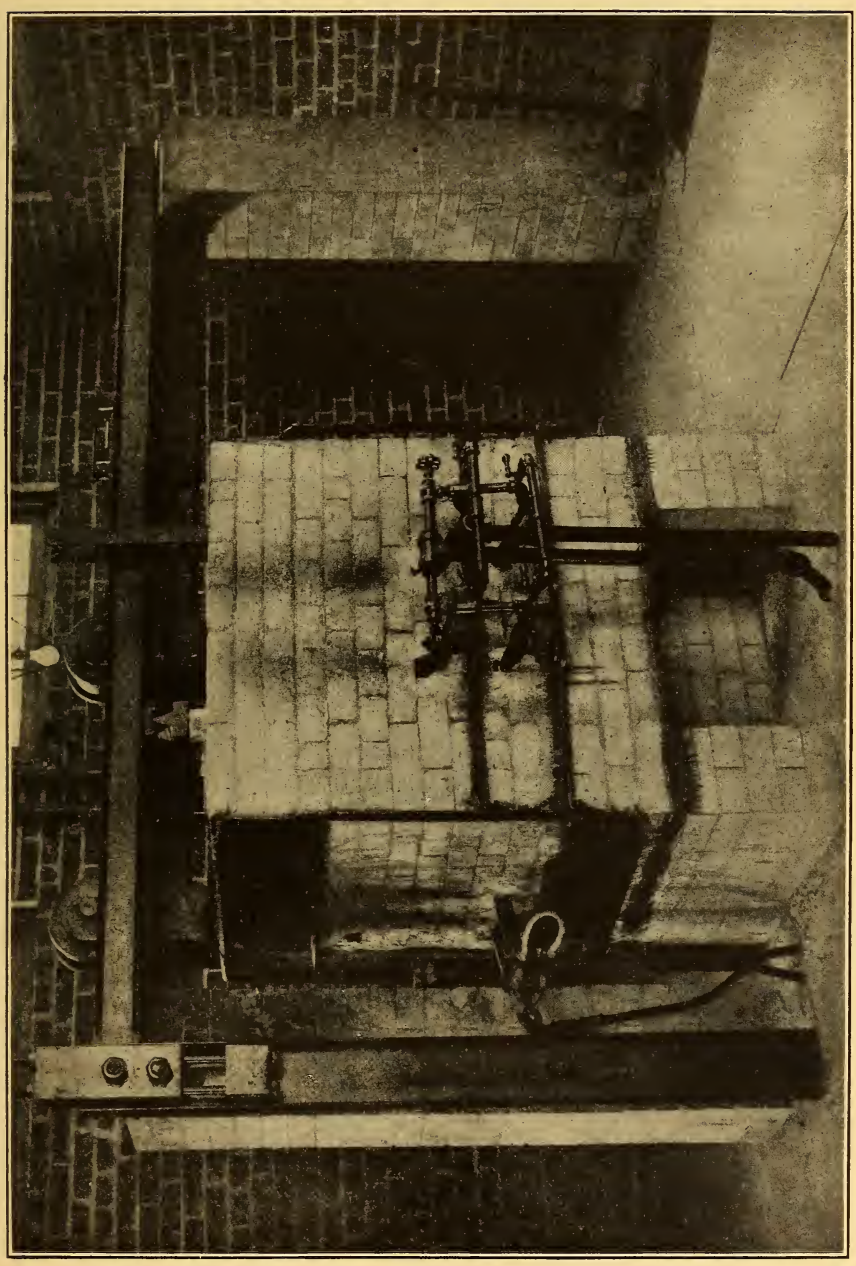

Fig. 16.—*The load-testing furnace at the Pittsburgh laboratory of the Bureau of Standards*

tubes immersed in a beaker of water, the temperatures of which were read regularly for making the necessary correction. Fig. 17 shows the time-temperature curves resulting from this test, which indicate that after 285 minutes, at the rate of heating followed

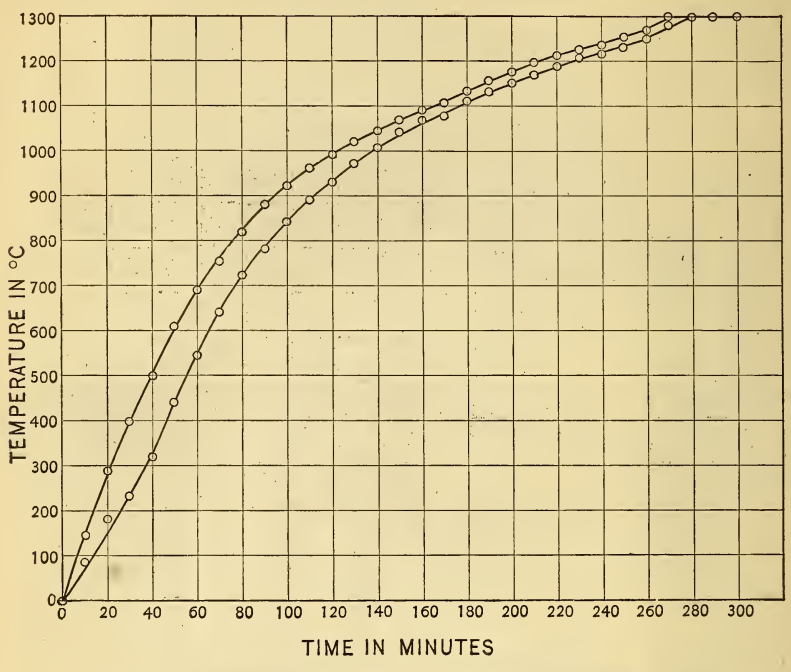

Fig. 17.—*Time-temperature curve of outside and inside of fire brick*

the temperature inside the brick was the same as that on the outside. Since it was necessary to conduct the test with reasonable rapidity, owing to the limited time during which power was available, the time-temperature curve shown in Fig. 18 was finally adopted.

In the course of this work more than 35 brands of fire brick were tested, as well as specimens made in the clay-products laboratory from different fire clays. Samples were obtained from

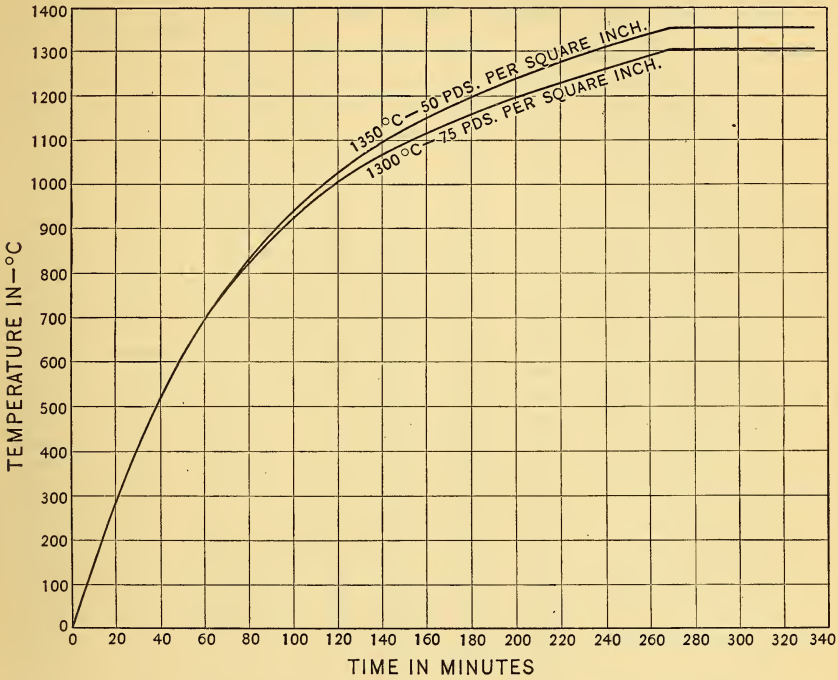

Fig. 18.—*Time-temperature plot of schedule adopted for the load tests*

manufacturers located in Pennsylvania, Maryland, Ohio, New Jersey, Missouri, Kentucky, and Colorado. For obvious reasons the names of the brands can not be given. The number of each material remains the same for all of the different tests.

TABLE V

Fire Brick and Clay Analyses

No.	SiO_2	Al_2O_3	FeO_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	H_2O at 100° C	Ignition loss	Total
1	81.60	14.55	1.15	0.49	0.37	0.27	0.67	1.08	.....	.....	.....	100.18
2	79.20	17.42	1.19	.49	.21	.38	.37	.91	.....	.....	.....	100.17
3	77.02	18.35	1.32	.52	.48	.28	.67	1.49	.....	.....	.....	100.13
4	54.58	37.35	4.10	1.57	.54	.53	.42	1.02	.....	.....	.....	100.11
5	54.70	39.72	1.32	1.86	.29	.52	.64	1.07	.....	.....	.....	100.12
6	54.69	38.86	1.41	1.92	.35	.52	.91	1.57	.....	.....	.....	100.23
7	54.25	38.90	1.83	1.92	.41	.78	.78	1.26	.....	.....	.....	100.13
8	52.30	41.52	1.28	2.46	1.02	.45	.28	.94	.....	.....	.....	100.25
9	63.89	29.28	2.05	2.40	.27	.29	.40	1.71	.....	.....	.....	100.29
10	60.37	34.83	1.37	2.05	.39	.31	.20	.67	.....	.....	.....	100.19
11	61.35	32.65	2.15	1.98	.46	.50	.17	.86	.....	.....	.....	100.12
12	55.66	36.52	2.59	2.40	.49	.61	.18	1.73	.....	.....	.....	100.18
13	68.73	25.12	2.26	1.32	.36	.49	.25	1.62	.....	.....	.....	100.15
14	60.77	32.63	2.89	1.94	1.12	.26	.26	.46	.....	.....	.....	100.33
15	56.55	36.64	2.84	1.90	1.34	.22	.32	.43	.....	.....	.....	100.25
16	50.76	44.24	1.45	2.03	.33	.29	.34	.60	.....	.....	.....	100.04
17	62.14	32.29	2.65	1.42	.71	.50	.13	.38	.....	.....	.....	100.22
18	62.74	31.80	2.45	1.53	.75	.56	.18	.18	.....	.....	.....	100.19
19	35.46	57.98	1.40	2.70	.29	.29	.75	1.30	.....	.....	.....	100.17
20	52.89	43.41	.90	2.12	.16	.13	.36	.27	.....	.....	.....	100.24
21	65.41	29.50	2.75	1.38	.45	.25	.10	.34	.....	.....	.....	100.18
22	66.53	28.66	2.35	1.36	.58	.42	.28	.19	.....	.....	.....	100.37
23	66.28	29.12	1.55	1.79	.59	.23	.27	.30	.....	.....	.....	100.13
24	77.82	19.00	1.01	1.65	.22	.06	.10	.28	.....	.....	.....	100.14
25	56.62	39.19	1.95	1.69	.36	.08	.18	.19	.....	.....	.....	100.26
26	54.51	40.42	1.90	2.46	.35	.17	.16	.20	.....	.....	.....	100.17
27	65.59	28.95	1.45	.93	.35	.60	.63	1.21	.....	.....	0.45	100.16
28	62.81	31.85	1.27	1.33	.28	tr	.53	1.72	tr	0.05	.30	100.14
29	68.15	26.30	1.97	1.10	.11	.23	.56	1.53	.....	.....	.25	100.20
30	65.34	30.01	1.45	.88	.18	.52	.38	1.21	.....	.....	.28	100.25
31	72.74	17.77	.80	1.55	.13	tr	.13	.27	.....	.18	6.55	100.12
32	56.69	29.48	1.20	1.87	.25	.12	.36	1.21	tr	.82	8.20	100.20
33	53.27	31.72	1.16	1.93	.21	.08	.30	.97	tr	.83	9.72	100.19
34	66.05	25.45	1.06	1.40	.20	.37	.30	1.05	tr	.23	4.05	100.16
35	58.88	26.41	1.35	1.22	.35	.42	.34	1.64	.01	.72	8.85	100.19
36	64.70	21.90	1.47	.86	.45	.60	.42	2.16	.02	.65	6.96	100.19
			FeO									
37	85.00	10.55	2.85	.42	.40	.43	.16	.....	.....	.....	.....	99.81
38	85.30	11.95	1.85	.30	.20	.29	.24	.....	.....	.....	.....	100.13
[60] 39	52.64	41.12	1.28	.74	1.23	.77	.55	.78	.....	.....	1.15	100.26

[60] A German fire brick of good quality.

TABLE VI

Chemical Formulas

No.	Al_2O_3	SiO_2	TiO_2	FeO	CaO	MgO	Na_2O	K_2O	Total RO
1	1.0	9.180	0.041	0.098	0.045	0.046	0.074	0.079	0.342
2	1.0	7.732	.036	.087	.022	.056	.035	.057	.257
4	1.0	7.140	.036	.092	.037	.038	.060	.088	.315
4	1.0	2.485	.054	.140	.026	.036	.019	.030	.251
5	1.0	2.343	.057	.042	.013	.033	.038	.043	.169
6	1.0	2.386	.064	.046	.016	.034	.038	.044	.178
7	1.0	2.365	.064	.060	.019	.051	.033	.035	.198
8	1.0	2.142	.075	.039	.045	.028	.011	.025	.148
9	1.0	3.710	.105	.089	.017	.025	.022	.063	.216
10	1.0	2.947	.075	.050	.020	.023	.009	.021	.123
11	1.0	3.196	.077	.064	.026	.039	.009	.029	.167
12	1.0	2.591	.085	.090	.024	.043	.008	.051	.216
13	1.0	4.651	.067	.115	.026	.050	.002	.070	.263
14	1.0	3.168	.076	.113	.063	.020	.013	.015	.224
15	1.0	2.634	.066	.099	.067	.015	.014	.013	.208
16	1.0	1.952	.059	.042	.014	.017	.013	.015	.101
17	1.0	3.294	.051	.104	.040	.039	.007	.013	.203
18	1.0	3.354	.061	.100	.043	.037	.009	.006	.195
19	1.0	1.040	.059	.031	.009	.013	.021	.014	.088
20	1.0	2.072	.062	.003	.004	.076	.016	.007	.106
21	1.0	3.770	.060	.119	.003	.022	.006	.013	.163
22	1.0	3.930	.060	.104	.037	.037	.016	.007	.201
23	1.0	3.871	.078	.069	.037	.020	.015	.011	.152
24	1.0	6.953	.111	.068	.021	.008	.009	.016	.122
24	1.0	2.458	.055	.063	.019	.005	.008	.005	.100
26	1.0	2.293	.078	.060	.016	.011	.007	.005	.099
27	1.0	3.850	.041	.064	.022	.052	.036	.045	.219
28	1.0	3.251	.052	.049	.015	tr	.027	.057	.148
29	1.0	4.410	.053	.095	.008	.022	.035	.063	.223
30	1.0	3.693	.037	.061	.011	.044	.021	.044	.181
31	1.0	7.000	.112	.058	.013	tr	.012	.017	.100
32	1.0	3.270	.081	.052	.015	.010	.020	.045	.142
33	1.0	2.854	.077	.047	.012	.006	.016	.033	.114
34	1.0	4.413	.070	.052	.014	.037	.019	.045	.167
35	1.0	3.789	.059	.065	.024	.040	.021	.067	.217
36	1.0	4.320	.043	.074	.037	.060	.032	.107	.310
37	1.0	13.680	.051	.377	.069	.103	.025	.....	.574
38	1.0	12.130	.032	.216	.030	.061	.033	.....	.340
39	1.0	2.18	.022	.040	.055	.047	.022	.020	.184

(d) **Accessory Tests.**—In addition to the load tests the following determinations were made:

1. Chemical analysis.
2. Crushing strength of the bricks on end in the cold condition.
3. Softening temperature.
4. Porosity.
5. True density.

Twenty bricks of each brand were secured and check determinations made.

1. For the purpose of the chemical analysis a sample sufficiently large was obtained by breaking up two half bricks and crushing them to pass the 100-mesh sieve. The disintegrated sample was allowed to flow in a small stream over a powerful magnet until all the particles of metallic iron were removed. The analyses were carried on under the supervision of Mr. P. H. Bates, chemist in charge of the Structural Materials Chemical Laboratory, by Mr. A. J. Phillips. The methods worked out by Dr. Hillebrand were used throughout this work.

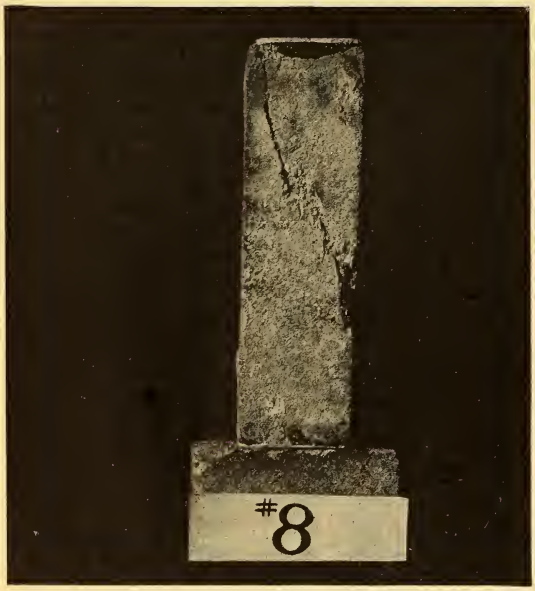

Fig. 19.—*Crushing test on a fire brick at ordinary temperature*

In Table V the chemical analyses of all the specimens tested are given and in Table VI the empirical chemical formulæ calculated from the analyses.

2. The crushing strength of the bricks, at ordinary temperatures, placed in the machine endwise, was determined in the usual way. Fig. 19 illustrates the appearance of a specimen after this

test, showing the sharp fracture. It was obviously necessary to make this test in order to establish the compressive strength of the fire bricks in the endwise position.

3. The softening temperature was obtained by chipping off specimens from the bricks and placing them in a Fletcher gas furnace, using preheated compressed air and natural gas. For the higher temperatures the small carbon resistance furnace illustrated by Fig. 4 was employed, in which a muffle consisting of a body containing 85 per cent of calcined alumina and 15 per cent of kaolin was first used. Later this composition was replaced by magnesite. This furnace was found very satisfactory. Seger-Orton cones were used for the estimation of the softening temperatures. The results were checked in each case.

4. The porosity was determined by obtaining the weight of a dry piece of the brick, the weight of the same specimen saturated with water by boiling in vacuo, and the suspended weight. The results checked practically with the porosity, calculated from the true and apparent densities.

5. The true density was obtained from 50-gram samples of the pulverized bricks, under the customary precautions as to the removal of air by boiling in vacuo and making corrections for the final temperature of the water.

(e) **Load Test.**—In carrying out the load test the beam is first raised as the temperature rises, due to the expansion of the furnace bottom and the brick; a quiescent stage is then reached, after which, from 1130° to 1290° C, a well-defined deflection begins, caused by the contraction of the brick. In some bricks this deflection continues at a very slow rate or reaches a state of equilibrium some time after the temperature has been raised to 1300° C. This kind does not fail under the conditions of the test, and the later deflection starts the more apt is the brick to stand up. The materials failing under the test show a more or less early start in settling, and the rate at which this takes place increases with the temperature, till finally it becomes so rapid that it is impossible to keep the beam level. Failure then is merely a matter of minutes and takes place very suddenly. In every case softening precedes failure.

TABLE VII

Results of Physical Tests at 1300° C and with a Load of 75 Pounds per Square Inch

No.	Dimensions, in inches, before	Dimensions, in inches, after	Linear compression, in inches	Deformation started	Cold crush-strength	Per cent porosity	Softening point in cones	Specific gravity
				°C				
1	9 by $4\frac{3}{8}$ by $2\frac{1}{2}$	Crushed	.....	1213	1464	30.2	28	2.671
2	9 by $4\frac{3}{8}$ by $2\frac{1}{2}$	Crushed	.....	1247	1289	30.1	28	2.638
3	$8\frac{7}{8}$ by $4\frac{1}{4}$ by $2\frac{1}{2}$	Crushed	.....	1210	989	32.4	28	2.635
4	9 by $4\frac{1}{2}$ by $2\frac{1}{2}$	Crushed	.....	1180	495	25.8	29	2.755
5	$8\frac{7}{8}$ by $4\frac{1}{4}$ by $2\frac{3}{8}$	$8\frac{1}{8}$ by $4\frac{1}{2}$ by $2\frac{9}{16}$	$\frac{3}{4}$	1191	1160	23.0	$31\frac{1}{2}$	2.732
6	9 by $4\frac{1}{2}$ by $2\frac{3}{8}$	$8\frac{1}{4}$ by $4\frac{1}{16}$ by $2\frac{7}{16}$	$\frac{3}{4}$	1213	931	22.9	31	2.691
7	9 by $4\frac{1}{2}$ by $2\frac{1}{2}$	$7\frac{3}{4}$ by $4\frac{9}{16}$ by $2\frac{5}{8}$	$1\frac{1}{4}$	1215	674	20.7	31	2.717
8	$8\frac{3}{4}$ by $4\frac{1}{4}$ by $2\frac{1}{2}$	$8\frac{3}{8}$ by $4\frac{1}{4}$ by $2\frac{5}{8}$	$\frac{3}{8}$	1295	1082	17.1	34	2.712
9	$8\frac{7}{8}$ by $4\frac{3}{8}$ by $2\frac{3}{8}$	Crushed	.....	1191	612	29.4	$29\frac{1}{2}$	2.674
10	$8\frac{7}{8}$ by $4\frac{1}{4}$ by $2\frac{1}{2}$	$8\frac{1}{2}$ by $4\frac{5}{16}$ by $2\frac{1}{2}$	$\frac{3}{8}$	1179	946	27.5	33	2.702
11	9 by $4\frac{1}{4}$ by $2\frac{1}{2}$	$7\frac{1}{2}$ by $4\frac{5}{8}$ by $2\frac{1}{2}$	$1\frac{1}{2}$	1133	480	25.1	28	2.678
12	9 by $4\frac{3}{8}$ by $2\frac{1}{2}$	Crushed	.....	1142	2614	24.5	$24\frac{1}{2}$	2.724
13	$8\frac{3}{4}$ by $4\frac{1}{2}$ by $2\frac{1}{2}$	Crushed	.....	1130	843	22.5	$28\frac{1}{2}$	2.664
14	$8\frac{7}{8}$ by $4\frac{1}{8}$ by $2\frac{1}{2}$	$8\frac{5}{16}$ by $4\frac{1}{4}$ by $2\frac{7}{16}$	$\frac{9}{16}$	1211	2226	25.5	$31\frac{1}{2}$	2.725
15	$8\frac{7}{8}$ by $4\frac{1}{4}$ by $2\frac{1}{4}$	$7\frac{7}{8}$ by $4\frac{3}{8}$ by $2\frac{7}{16}$	1	1234	1638	23.1	31	2.705
16	9 by $4\frac{3}{8}$ by $2\frac{1}{2}$	8 by $4\frac{1}{2}$ by $2\frac{9}{16}$	1	1205	971	24.3	34	2.712
17	$8\frac{3}{4}$ by $4\frac{1}{4}$ by $2\frac{3}{8}$	$8\frac{7}{16}$ by $4\frac{3}{8}$ by $2\frac{1}{2}$	$\frac{13}{16}$	1233	2578	23.9	31—	2.712
18	$8\frac{7}{8}$ by $4\frac{1}{4}$ by $2\frac{1}{2}$	$8\frac{3}{16}$ by $4\frac{9}{16}$ by $2\frac{1}{2}$	$\frac{13}{16}$	1274	955	21.0	32	2.647
19	$9\frac{1}{8}$ by $4\frac{1}{2}$ by $2\frac{1}{2}$	$8\frac{1}{2}$ by $4\frac{9}{16}$ by $2\frac{1}{2}$	$\frac{5}{8}$	1235	2071	33.3	33+	2.975
20	$8\frac{3}{4}$ by $4\frac{1}{4}$ by $2\frac{1}{2}$	$8\frac{1}{2}$ by $4\frac{7}{16}$ by $2\frac{1}{2}$	$\frac{1}{4}$	1213	2005	26.8	31	2.738
21	$8\frac{7}{8}$ by $4\frac{1}{4}$ by $2\frac{1}{2}$	$8\frac{9}{16}$ by $4\frac{3}{8}$ by $2\frac{7}{16}$	$\frac{5}{16}$	1231	3174	22.2	31	2.668
22	$8\frac{7}{8}$ by $4\frac{1}{4}$ by $2\frac{1}{2}$	$8\frac{1}{4}$ by $4\frac{3}{8}$ by $2\frac{9}{16}$	$\frac{5}{8}$	1234	2191	26.8	31	2.676
23	$8\frac{7}{8}$ by $4\frac{3}{8}$ by $2\frac{1}{2}$	$8\frac{5}{16}$ by $4\frac{5}{16}$ by $2\frac{1}{2}$	$\frac{9}{16}$	1264	4234	23.9	31	2.677
24	9 by $4\frac{3}{8}$ by $2\frac{1}{2}$	$8\frac{7}{8}$ by $4\frac{3}{8}$ by $2\frac{1}{2}$	$\frac{1}{8}$	0	2551	27.5	29	2.622
25	9 by $4\frac{1}{4}$ by $2\frac{3}{8}$	$8\frac{3}{4}$ by $4\frac{1}{4}$ by $2\frac{9}{16}$	$\frac{1}{4}$	1291	1241	26.3	$31\frac{1}{2}$	2.702
26	$8\frac{7}{8}$ by $4\frac{1}{4}$ by $2\frac{1}{2}$	$7\frac{5}{8}$ by $4\frac{1}{2}$ by $2\frac{1}{2}$	$1\frac{1}{4}$	1207	1138	22.3	31	2.744
27	8 by $3\frac{3}{4}$ by $2\frac{1}{4}$	Crushed	.....	1168	4042	18.1	26	2.682
28	9 by $4\frac{1}{2}$ by $2\frac{5}{8}$	$8\frac{5}{8}$ by $4\frac{1}{2}$ by $2\frac{5}{8}$	$\frac{3}{8}$	1215	2509	27.4	$31\frac{1}{2}$	2.643

With another kind of material (of silicious composition, low in fluxes) the rise in height remains stationary for some time, followed by a long quiescent period. After the maximum temperature is reached a very slow and gradual settle takes place which is quite small and decreases in rate as the temperature is kept constant. Such materials remain perfectly straight and shrink but a small amount.

Undoubtedly some of the bricks tested would have been deformed badly on long time tests which it was impossible to

carry out under the conditions of the plant, but in several cases where the time of testing was extended considerably a kind of equilibrium was reached, after which no observable changes took place. It is very likely that in these cases solution of the more refractory portion of the brick took place which stiffened up the bonding material.

(f) **Results of the Load Test Series, 75 Pounds Per Square Inch at 1300° C.**—The results of the physical tests of this series are arranged in Table VII. Typical failures are shown by the halftones, Figs. 20 and 21, and the condition of bricks which stood up well is illustrated by Fig. 22.

Fig. 20.—*Failures of specimens Nos. 1 and 2*

It appears from the photographs that where the bricks were badly distorted and crushed in each case a certain degree of softening took place, as is clearly indicated by the curved surfaces. It is evident that these bricks attained a viscous condition, in which they were not able to carry the load imposed upon them, though the latter is small as compared with the crushing strength at the atmospheric temperature, which for the 26 samples tested averaged 1520 pounds per square inch. Inspection of the failures shows plainly that the more refractory flint clay has not softened to the slightest extent. The grains have lost none of their orig-

inal identity. They seemed to have slid upon each other, the bond clay behaving analogously to a lubricant. From this it follows that no matter how excellent the major constituent of the brick may be as to refractoriness, if the bond clay is too deficient in this respect the load-carrying power of the product is impaired. In other words, as far as this property is concerned a fire brick is not any better than its weakest constituent, *unless the mass is made homogeneous by finer grinding and blending.*

It is observed that there is some rough relation between the softening temperature and the ability of the bricks to stand up

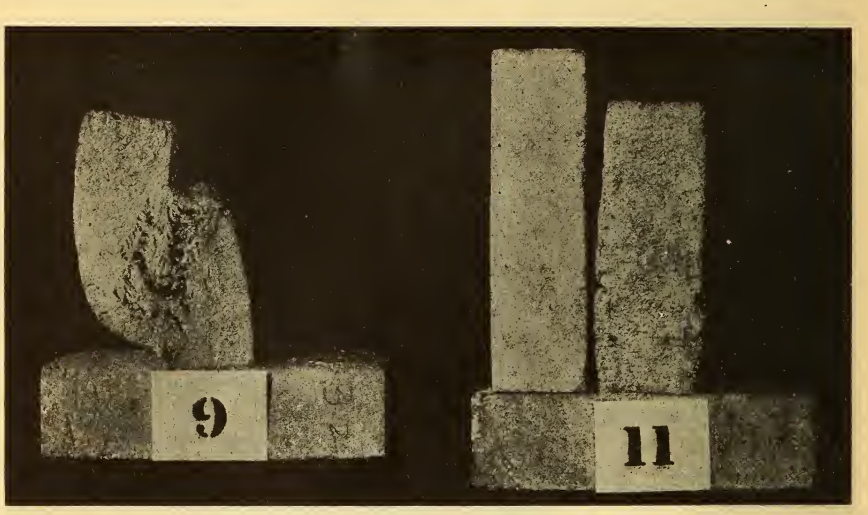

Fig. 21.—*Failures of specimens Nos. 9 and 11*

under the test, but it is also seen that this is not true unqualifiedly. Test No. 16 is one of the decided exceptions. The materials which have failed not only show a softening point below cone 30, but also a certain high content of fluxes. On the other hand, while a brick may soften below cone 30, if its content of RO constituents is low it will resist the conditions of the load test without difficulty. In No. 24 we have an illustration of this kind, and many silica bricks show similar results. Nevertheless it seems quite clear that the load test in a measure is a determination of the refractoriness in spite of the low temperature at which it is conducted.

In Fig. 23 the failures due to the crushing of the bricks under the load of 75 pounds per square inch at 1300° C are plotted with reference to chemical composition and it is observed at once that the most significant factor seems to be the RO content. It is not to be expected that a sharp division line exists between the area of failure and that of satisfactory load carrying ability, since in some cases the FeO, which constitutes part of the RO, may be present in the form of larger grains, in which condition it is not so detrimental. The fact is again shown that neither the softening temperature nor the chemical analysis alone produces the infor-

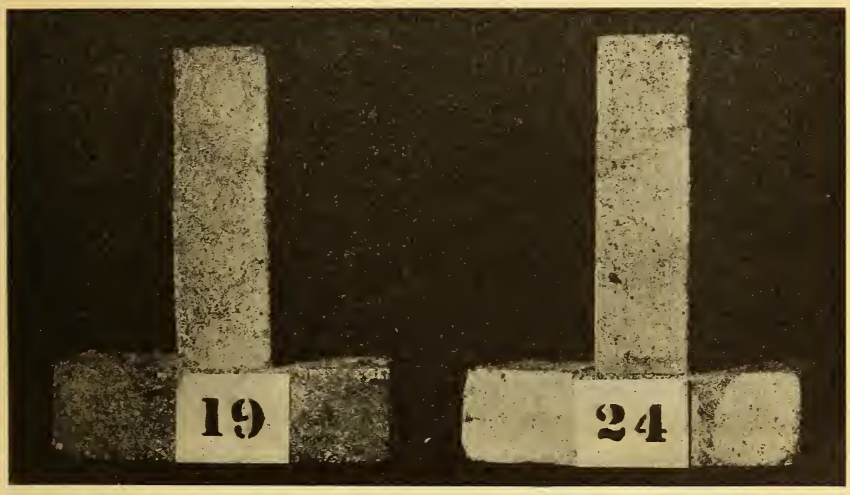

Fig. 22.—*Result of load test upon specimens Nos. 19 and 24*

mation brought out by the load test. Given all three of these data, however, a very good presentation of the heat resistance of a fire brick is obtained.

(g) **Effect of Chemical Composition.**—Examining the question from the chemical standpoint and assuming that the fire brick body consists of a refractory constituent corresponding in composition to the kaolin formula and of a more fusible cementing component, the following method might be pursued to show theoretically the make-up of the mixture. Taking, for example, one of the failures, say sample No. 4, and calculating the empirical

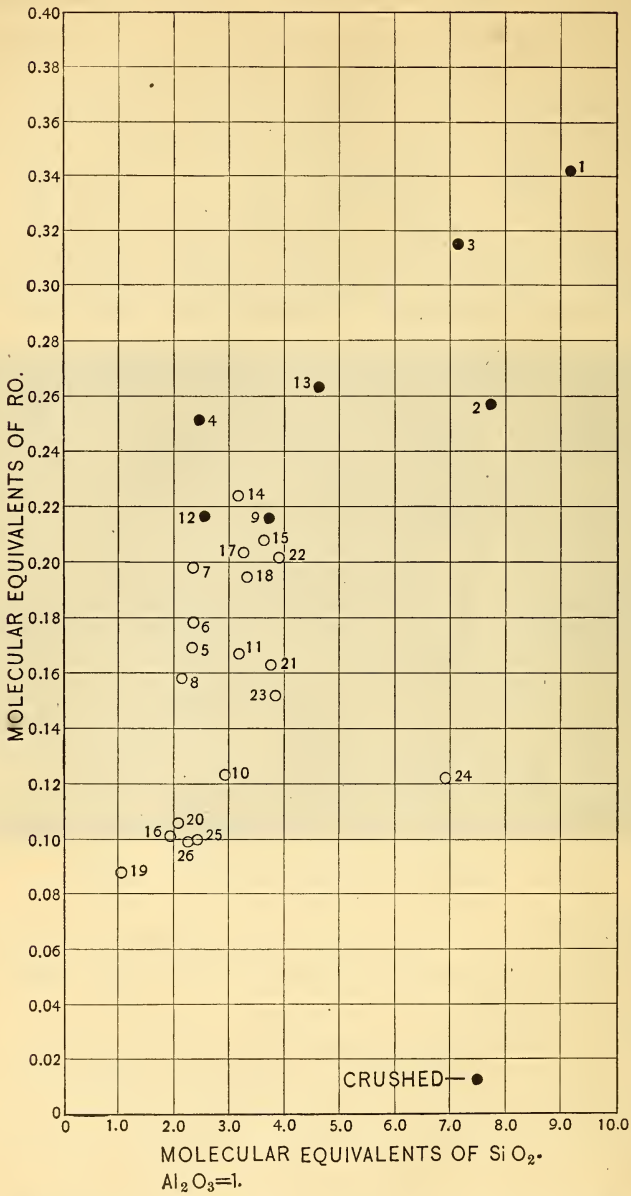

Fig. 23.—*Diagram showing RO : SiO_2 relation with reference to failure under the conditions : 1300°C and 75 pounds per square inch*

formula, the latter is found to be: 0.019 Na_2O, 0.030 K_2O, 0.036 MgO, 0.026 CaO, 0.14 FeO, 0.054 TiO_2, 1.00 Al_2O_3, 2.485 SiO_2. Upon the assumption that the alkalies are derived from orthoclase feldspar the molecular equivalents of the latter would be 0.019 + 0.030 = 0.049. Deducting the alumina belonging to the feldspar from 1 we obtain 0.951 equivalent Al_2O_3 present as clay substance, which corresponds to 1.902 equivalent of SiO_2. Subtracting this from 2.485 leaves 0.583 equivalent silica. Multiplying the equivalents by the respective molecular weights and reducing to the percentage basis we find the following distribution of clay substance, feldspar, and free silica:

	Per cent
Clay substance	77.23
Feldspar	10.06
Fluxes and free silica	12.71

This shows an excessive amount of fluxing material in proportion to the clay base, but the case is still more striking, since the composition of the fluxes and the free silica upon calculation reduces to the formula (using RO = 1, as is customary for slags and glasses): RO 1.43 SiO_2 . 0.267 TiO_2. This represents a slag which is not saturated with silica at the temperatures involved and hence it is certain to attack the clay substance, thus bringing into solution still more material and increasing the proportion of fusible to refractory constituents. In this theoretical consideration we must keep in mind that the effect is more marked owing to the heterogeneous mixture of the assumed pure clay and the impure bond clay, in which the particles of the former might be imagined to float in the latter. The more thoroughly the two materials are ground and blended together the better would the body behave in the load test, until finally the effect would be that corresponding to a single clay of the average composition, though even in this case it would remain a somewhat inferior material, owing to the high content of fluxes. The more impure the bond clay, therefore, the more complete and intimate should be be the mixture.

From the above consideration the behavior of this body in the load test is, therefore, not surprising.

(h) **Influence of the Cold-Crushing Strength.**—A comparison of the initial, cold, crushing strength and the load behavior shows no apparent connection, but the fact is brought out that low

initial strength is a handicap. Bricks Nos. 4 and 11 are examples of this kind. While No. 4 would have failed irrespective of its cold crushing strength, the failure was more complete on account of its weakness, and No. 11 in all probability would have shown a very much smaller condensation; in fact, it might have stood the test.

The hardness of burning in general is a factor worthy of consideration. Although firing to a high temperature can not, in the nature of the case, effect any fundamental change, and can not convert a low-grade material into a good one, our work has shown that well-burnt bricks stand up better than soft-burnt products. This is due, not only to the greater compactness of the body, but also the change in the composition of the bonding material where such is used. In other words, hard burning will cause the usually decidedly less refractory, plastic clay to dissolve some of the fine part of the better material (flint clay), thus increasing its own refractoriness and hence its resistance to load conditions. For instance, No. 26 would have shown up better if it had been burnt harder.

The pore space of fire bricks, in the nature of the case, is more open than that of other clay products. This is shown by the fact that the porosity determined by water absorption agrees practically with the porosity calculated from the true and lump densities of the specimens. The true density of the different samples has no particular significance, except that the inferior refractories have a tendency to show lower specific gravities.

The decided variations in crushing strength (at atmospheric temperature) which are observed seem to indicate widely varying conditions as to the initial water content employed in slop molding, and there is no doubt but that there is considerable room for improvement with regard to the development of greater mechanical strength by proper grinding and pugging.

10. RESULTS OF THE TESTS AT 1350° C AND WITH A LOAD OF 50 POUNDS PER SQUARE INCH

(a) **Comparison with Results of 1300° Test.**—The results of this series are compiled in Table VIII.

It is observed that not all of the 1300-degree load tests were repeated, but only a sufficient number to establish the relative

severity of each condition. Such cases were selected in which a difference in behavior might be expected.

In comparing the data obtained in the two series it was found that the results were approximately the same, with the exception that the 1350-degree 50-pound tests appeared to be somewhat more sensitive and differentiated more sharply between the various kinds of refractories. This is shown by the fact that while a certain brand of brick failed in the lower temperature test by excessive contraction it failed at the higher temperature by collapsing. Also the compression effect in the second test was found to be somewhat

Fig. 24.—*Comparison of specimen No. 12 under the two conditions of the load test. B refers to the 1350° test*

greater than in the first test. In one case the compression was greater in the 75-pound than in the 50-pound test. In this connection account must be taken of the fact that the samples were selected from stock, and two bricks of the same stock do not necessarily possess identical composition.

Both tests, however, condemned inferior materials with practically equal certainty.

In Fig. 24 the failure of sample No. 12 in the 1300° and 1350° C is illustrated. Both conditions have brought about the same effect.

Again, Fig. 25 shows the appearance of No. 13 in the two series of tests. The specimens failed in both tests, but the effect of the higher temperature seemed to have been more potent in bringing about the collapse of the bricks.

The pressure effect appears to be more prominent in the 1300-degree 75-pound series, while under the second conditions the softening due to heat is more pronounced. There is more deformation in the sense of flow in the 50-pound series.

It is again evident that this test not only is useful in determining the load-carrying ability at furnace temperatures, but also

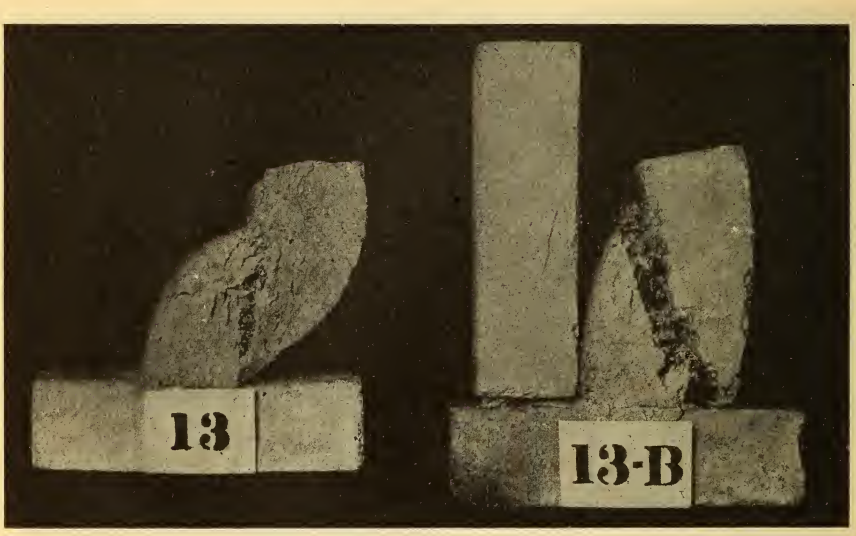

Fig. 25.—*Comparison of specimen No. 13, under the two conditions of testing*

serves as a measure of the refractoriness of a certain product. In considering furnace conditions it is at once evident that everywhere pressures are to be resisted and not only those due to loads, but also the compression and tension stresses caused by thermal expansion and contraction. The higher the furnace temperature the more rapidly is the load-carrying ability reduced until finally the refractory is unable to support its own weight.

The load test, therefore, measures the viscosity of the fire-clay bodies at a certain temperature. Since any good refractory should possess sufficient rigidity at the temperature at which it is to be

used to carry the load or to resist the pressure it is called upon to meet, it is evident that a fire brick lacking in this respect is as inferior as a material showing a low softening temperature.

TABLE VIII

Results of Physical Tests at 1350° C and with a Load of 50 Pounds per Square Inch

No.	Dimensions, in inches, before	Dimensions, in inches, after	Linear compression, in inches	Deformation started	Cold crush-strength	Per cent porosity	Softening point in cones	Specific gravity
				°C				
2 B	9 by $4\frac{3}{8}$ by $2\frac{3}{8}$	Crushed	.....	1220	1289	30.1	28	2.638
4 B	$8\frac{7}{8}$ by $4\frac{3}{8}$ by $2\frac{1}{2}$	Crushed	.....	1175	495	25.8	29	2.755
7 B	$8\frac{7}{8}$ by $4\frac{3}{8}$ by $2\frac{3}{8}$	$8\frac{1}{8}$ by $4\frac{3}{8}$ by $2\frac{1}{2}$	$\frac{3}{4}$	1218	674	20.7	31	2.717
9 B	9 by $4\frac{1}{4}$ by $2\frac{1}{2}$	Crushed	.....	1238	612	29.4	$29\frac{1}{2}$	2.674
11 B	$8\frac{7}{8}$ by $4\frac{3}{8}$ $2\frac{3}{8}$	Crushed	.....	1165	480	25.1	28	2.678
12 B	9 by $4\frac{3}{8}$ by $2\frac{3}{8}$	Crushed	.....	1175	2614	24.5	$24\frac{1}{2}$	2.724
13 B	$8\frac{3}{4}$ by $4\frac{1}{4}$ by $2\frac{1}{2}$	Crushed	.....	1150	843	22.5	$28\frac{1}{2}$	2.664
15 B	$8\frac{7}{8}$ by $4\frac{1}{4}$ by $2\frac{1}{2}$	$7\frac{3}{4}$ by $4\frac{1}{2}$ by $2\frac{1}{2}$	$1\frac{1}{8}$	1245	1638	23.1	31	2.705
19 B	$9\frac{1}{16}$ by $4\frac{7}{16}$ by $2\frac{1}{16}$	$8\frac{1}{2}$ by $4\frac{1}{2}$ by $2\frac{9}{16}$	$\frac{9}{16}$	1200	2071	33.3	33+	2.975
20 B	$8\frac{7}{8}$ by $4\frac{1}{4}$ by $2\frac{1}{2}$	Note: 4 hours at 1350°	$\frac{7}{8}$	.....	2005	26.8	31	2.738
23 B	$8\frac{7}{8}$ by $4\frac{3}{8}$ by $2\frac{1}{2}$	$8\frac{1}{8}$ by $4\frac{1}{2}$ by $2\frac{1}{2}$	$\frac{3}{4}$	1290	4234	23.9	31	2.677
26 B	9 by $4\frac{1}{4}$ by $2\frac{1}{2}$	8 by $4\frac{3}{8}$ by $2\frac{1}{2}$	1	1220	1138	22.3	31	2.744
29	9 by $4\frac{1}{4}$ by $2\frac{1}{2}$	Crushed	.....	1230	4714	22.2	29	2.627
30	$8\frac{1}{2}$ by $4\frac{1}{4}$ by $2\frac{1}{4}$	Crushed	.....	1180	1585	27.9	$26\frac{1}{2}$	2.653
31	$8\frac{7}{8}$ by $4\frac{3}{8}$ by $2\frac{3}{8}$	$8\frac{5}{8}$ by $4\frac{1}{2}$ by $2\frac{3}{8}$	$\frac{1}{4}$	1250	1054	30.6	30	2.654
32	8 by $3\frac{3}{4}$ by $2\frac{1}{8}$	$7\frac{1}{2}$ by $3\frac{7}{8}$ by $2\frac{1}{8}$	$\frac{1}{2}$	1330	2829	32.5	31	2.565
33	$7\frac{7}{8}$ by $3\frac{3}{4}$ by 2	$7\frac{3}{8}$ by $3\frac{3}{4}$ by 2	$\frac{1}{2}$	1330	9008	12.4	32	2.655
34	$8\frac{1}{4}$ by 4 by $2\frac{1}{4}$	Crushed	.....	1180	7819	7.4	25	2.521
35	$8\frac{7}{16}$ by 4 by $2\frac{1}{8}$	$7\frac{9}{16}$ by 4 by $2\frac{1}{8}$	$\frac{5}{8}$	1280	7404	12.0	$30\frac{1}{2}$	2.618
36	$8\frac{1}{2}$ by 4 by $2\frac{1}{4}$	Crushed	.....	1200	4368	17.4	$27\frac{1}{2}$	2.649
37	$8\frac{3}{4}$ by $4\frac{1}{4}$ by $2\frac{1}{2}$	Crushed	.....	1180	1725	23.8	29	2.490
38	9 by $4\frac{1}{2}$ by $\left\{\begin{matrix}3\frac{3}{4}\\2\end{matrix}\right.$	Crushed	.....	1150	1910	23.8	29	2.575
39	$4\frac{1}{2}$ by $2\frac{5}{16}$ by 3	$4\frac{15}{32}$ by $2\frac{5}{16}$ by 3	$\frac{1}{32}$	.....	.....	.....	$33\frac{1}{2}$	.....

(b) **Influence of Change in Shape of Test Specimen.**—It was thought advisable to make some tests involving changes in the shape of the test specimens. Thus, Fig. 26 shows a small pier built up of four half bricks, representing a brand, No. 12, which had failed in the usual tests. (See Fig. 24.) The half bricks were laid up solidly in good fire-clay mortar and then subjected to the

load of 50 pounds per square inch at 1350° C. The photograph shows that failure occurred very similarly to that observed in the previous tests of the same brand of bricks.

(c) **Illustration of the Value of the Load Test.**—As an illustration of the application of this test to the testing of refractories the following case might be cited: A lot of coke-oven brick pur-

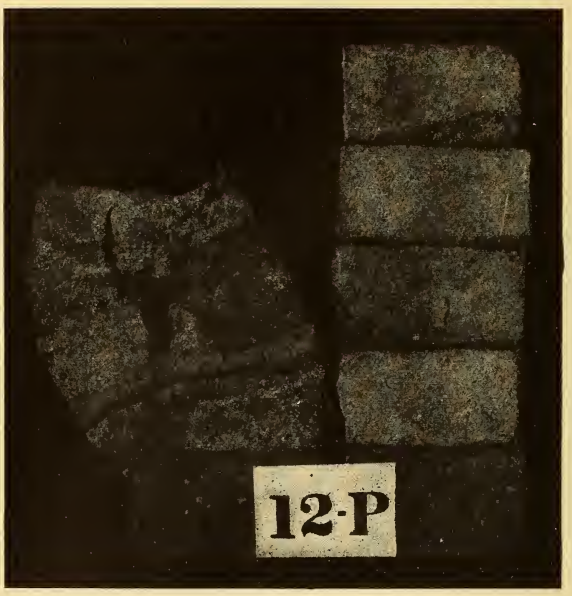

Fig. 26.—*Failure of small pier built up of specimen No. 12, at 1350° and 50 pounds per square inch*

chased by the Jones & Laughlin Steel Co., of Pittsburgh, and used in their ovens, proved to be very unsatisfactory. At the request of this company some of these bricks were submitted to the load test. When subjected to the conditions of series B, the samples failed utterly long before the final temperature was reached, as is illustrated by Fig. 27.

11. GENERAL RESULTS OF LOAD TESTS

(a) **Limit of RO Content.**—In Fig. 28 all of the load tests made so far under both conditions are incorporated in the chart, showing the RO and SiO_2 contents expressed in molecular equivalents. The alumina is, of course, equal to unity. It is observed that while failures occur even with as low as 0.17 equivalent of RO this applies to a siliceous material in which the fluxes appear to be more effective, as has been pointed out by Richters in his tests of 40 years ago. On the other hand, no material seems to stand up which contains more than 0.225 equivalent of RO.

The more siliceous a material is the lower should be the content of fluxes. However, a sufficient number of high silica samples were not at hand to fix the rate at which the RO content should diminish with increase in silica. The increased effect of the fluxes in siliceous material is, however, clearly indicated by the dotted line shown in the diagram.

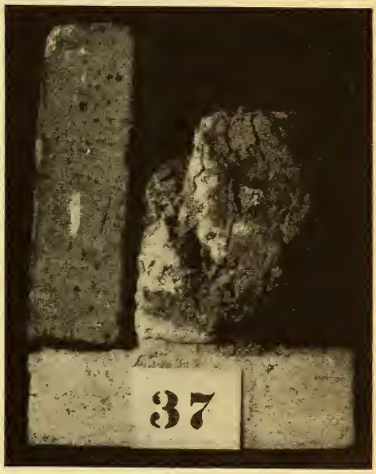

Fig. 27.—*Failure of a coke-oven brick which proved to be unsatisfactory in practice, tested at 1350°, 50 pounds per square inch*

Owing to the fact that the chemical analyses made for this work under the direction of Mr. P. H. Bates, of the Pittsburgh laboratory, Bureau of Standards, have been made with great care, the diagram represents relations of some importance.

(b) **Fairness of the Load Test.**—There is yet to be met the question whether the load test is fair to all kinds of refractories and what the exact conditions are to be.

Study of the results obtained shows that the test in which the temperature is 1350° C and the load 50 pounds per square inch is to be preferred. The main purpose of this work has been to suggest a test for high-grade refractories which would with certainty reject

any lower grade material. It has been successful in doing this, but whether it is too severe remains to be seen. In no case should a refractory be condemned solely on the basis of this test unless it has been established that the material is to be used under load conditions. At any rate, the softening temperature should be

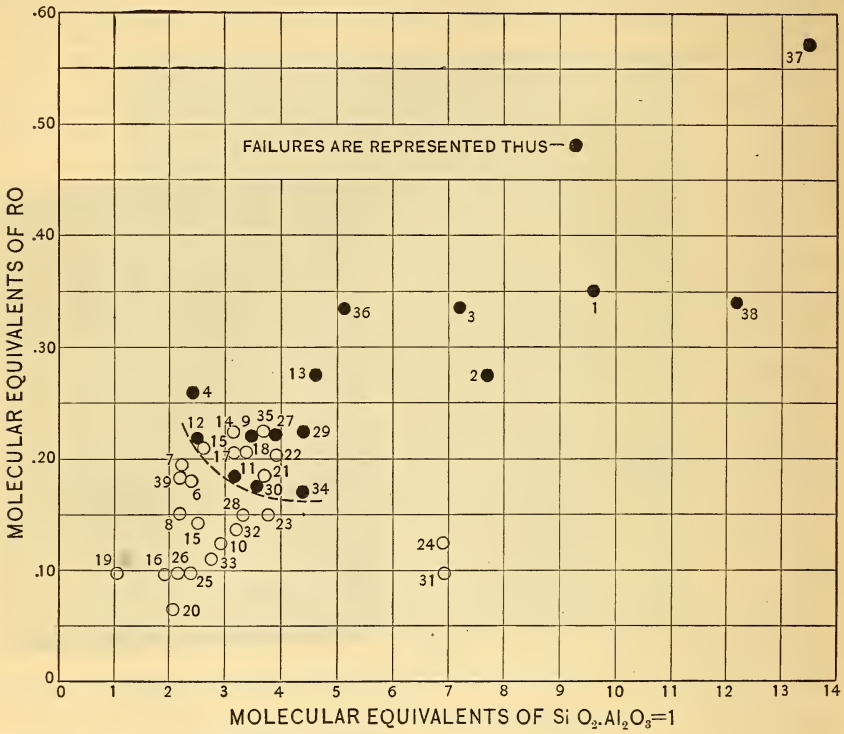

Fig. 28.—*Diagram showing RO-SiO_2 relation of all specimens tested, referring to both conditions of testing*

determined and a chemical analysis should be made to serve as supplementary evidence.

In the possession of these three kinds of data it should not be a difficult matter to determine whether or not the refractory is a No. 1 material.

12. TESTS OF AN IMPROVED FIRE-CLAY BODY

In order to illustrate the point brought out as regards the improvement of the bond clay by adding to it some flint clay or other high refractory and grinding the mixture in a machine like the ball mill, a test was carried out along this line. A plastic clay of the No. 2 type was taken to represent an inferior bond clay. This material possessed a softening point of cone 27½, and when made up into bricks and subjected to the load test it failed com-

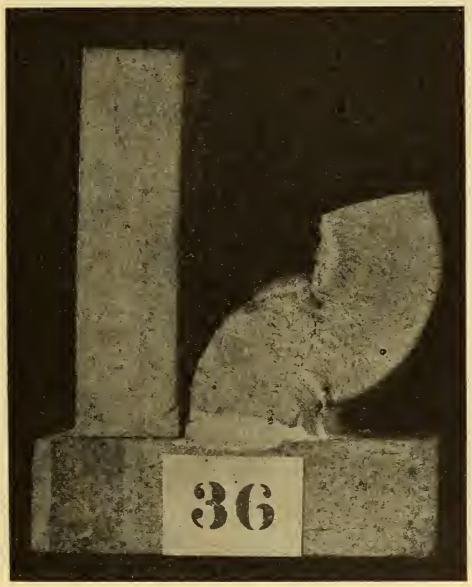

Fig. 29.—*Failure of brick No. 35, made from plastic fire clay*

pletely, as is shown by Fig. 29. In order that the distortion might not be too complete, the test conditions were modified in this special case by using a temperature of 1300 degrees and the load of 50 pounds per square inch. Another set of bricks was then made, consisting of 70 per cent of this clay and 30 per cent of high-grade flint clay, ground together in a ball mill to pass the 20-mesh sieve. The brick made from both the clay and the mixture were fired to cone 12. In Fig. 30 the appearance of the bricks made from the

mixture is shown under the same testing conditions obtaining for the first series. The improvement thus brought about is obvious, and an example is thus afforded of how inferior bond clays may be improved by intimate grinding with a refractory of good quality. By improving the standing-up behavior of the bond clay, even though somewhat more of the bond mixture must be used, and adding the additional flint clay in the usual manner, it is evident that the refractory quality of the fire bricks is decidedly

Fig. 30.—*Result of load test upon a brick made from 70 per cent flint clay and 30 per cent plastic clay, ground together in ball mill*

improved. In this manner it is perfectly possible to make use of clays of the kaolin type to strengthen the plastic bond.

13. GENERAL CONCLUSIONS BASED UPON RESULTS OF LOAD TESTS

(a) **Refractories Made from One Clay.**—As to fire bricks made from a clay material which is sufficiently plastic so that no bonding clay is necessary, it is clear that its ability to carry loads depends simply upon the composition. Some of the very best tests have been obtained from materials of this kind. This case is the

simplest and needs no particular discussion, since a clay will stand up or fail by virtue of its own quality. A pure clay of moderate plasticity would be the ideal material for the manufacture of fire bricks. Since, however, such clays are usually not available, the question of judging them deserves some attention from the standpoint of load-carrying capacity. From this point of view the most important consideration is that of the amount of fluxes.

At the high temperature involved the presence of even a small amount of fluxes becomes a potent factor, and hence it is far better to select a clay higher in silica and low in fluxes than one possessing the silica-alumina ratio of kaolin but higher in fluxes. An increase in silica, while it does lower the ultimate softening point, *with low fluxes*, may not cause the material to be inferior for actual work. However, high silica and high fluxes make a dangerous combination. From this it follows that a clay fairly high in fluxes, corresponding, for instance, to $0.22\ RO\ .\ Al_2O_3\ .\ 2\ SiO_2$, would be improved by the dilution with a siliceous material containing practically no fluxes, or even by the addition of a clean sandstone, the principal requirement being intimate blending and grinding. In other words, the diluting effect of the silica due to its lack of fluxes overbalances the decrease in ultimate refractoriness caused by the addition of silica.

In regard to the fluxes present in a clay the state and size of grain of the iron is of importance, for it is evident that coarser grains of iron minerals will do no harm, though in the analysis they contribute their share toward raising the amount of flux. An effort should be made to determine the amount of such grains and to make the proper correction in reporting the analytical result.

The fluxes are an important factor in the ability of refractories to carry loads, inasmuch as they become active at low temperatures by forming easily fusible silicates. As the temperature rises increasing amounts of silica and alumina are dissolved, and it becomes therefore simply a matter of the amount of this softened matter and its viscosity whether or not a given refractory will stand up at the temperature in question. As the temperature rises or the load is increased a point is reached where the entire body becomes too viscous to retain its shape.

By grinding the clay as coarse as possible conditions are improved, as in doing this the formation temperature of the fusible silicates is raised, since the process of solution is delayed, and by these means it may be possible to bring the product out of the danger zone. Owing to the slow rate at which conditions of equilibrium are approached but never reached, this point has some practical importance. In time, however, it might be possible that a brick may fail under the same conditions under which it stood up at first.

The question of grog is likewise an important one in this connection. Its function from the standpoint of load-carrying ability is twofold: By proper sizing it may be made to improve the mechanical strength of the product; by using grog consisting of high-grade clay and grinding part of it fine, the standing-up quality is improved.

(b) **Refractories Made from Flint and Bond Clay.**—In this case we are dealing with comparatively coarse grains of flint and fine grains of bond clay. These two materials are mixed and blended as far as the processes customary at the present time permit it. The bond clay breaks up more readily, and the plastic mass produced by it cements together the grains of flint clay and calcine. To a large extent the load-carrying capacity of the product depends upon the bond, as has been shown above. It is evident that if the flint clay is inferior the product suffers accordingly. From previous considerations it is clear that the bond clay should have as low a porosity-temperature gradient as possible; i. e., the temperature at which it becomes dense and nonabsorbent should be as high as possible. As to fineness of grain, it might be said that the grinding should not be carried any further than is necessary to develop good plasticity.

(c) **Improvement of Bond Clay.**—If a flint-bond clay mixture should prove unsatisfactory as regards its ability to carry loads, the first step would be to cut down the amount of plastic clay, if possible. If this should not be feasible or beneficial, the plastic material would be improved by grinding it intimately with a portion of the flint clay to such a degree of fineness as would insure thorough incorporation. This could be done by dry or, preferably, wet grinding. In the latter case it might be possible to pug the

additional, coarser flint clay into the slip, which naturally would be maintained thick as possible. The finely ground flint clay would not remain inert, but would be certain to develop some plasticity.

Another alternative would of course be the substitution of another clay for the unsatisfactory plastic bond. Since not infrequently siliceous clays are at hand this might prove feasible, even though the amount of bonding material would have to be increased. Where the flint clay is becoming scarce it might be possible to find some clean, soft sand rock which could be ground into the plastic bond clay and which would thus improve its behavior under load conditions.

By some such means as have been indicated here it would not seem a difficult matter, in most cases, to manufacture products fulfilling all reasonable requirements as to crushing strength at the usual furnace temperatures. In addition, by paying attention to the sizing of the ground clays, so as to produce as dense a structure as possible, by the use of less water or by adopting dry pressing, the load-carrying capacity of the fire bricks would be increased. Likewise, burning at as high a temperature as possible assists in bringing about the same result. Experiments carried on by the writers have shown that harder burning has increased the strength of fire bricks appreciably. With reference to this point it might be said that refractories can not be fired at too high a temperature. The superiority of high-fired over low-fired ware from every standpoint, especially as regards change in volume when part of the furnace wall is so striking, that every effort should be made to push to the maximum possible burning temperature.

Unfortunately, the users of refractories do not realize the cost of producing high-grade ware, but insist upon low prices, which do not permit the manufacturers to exercise that care in the selection, mixing, sizing, and burning of the products which is necessary for the best results. It is self-evident that this is poor policy, as the initial cost of the refractories is very small as compared with that of repairs and the loss caused by shutdowns. As soon as the users are ready to pay satisfactory prices for high quality they will have no trouble in securing high-grade products from American manufacturers. The fire clays of this country are not surpassed in

quality by those of Europe, contrary to certain existing prejudices, and our refractory industries are not lacking in progressiveness in using them.

14. CLAY FIRE BRICK SPECIFICATION

(a) **Influence of Furnace Conditions.**—The difficulty of writing specifications for refractories is at once realized when one considers the various conditions which may affect the materials in use. Not only the internal changes going on within the fire-clay product, such as the crystallization of sillimanite and the expansion due to the continued formation of tridymite, which bring about changes in volume and hence cause strains, but also the external agencies affecting them vary widely.

Then there is the effect of ashes in coal-fired furnaces, consisting both in mechanical abrasion and slagging, the fluxing and dissolving action of glass in tanks and pots and of slags, the sudden heating and cooling of regenerator checkerwork, the abrading action of ore and flux in blast furnaces, the effect of dust, etc. In addition peculiar reactions must be dealt with under certain conditions, such as the reducing action of carbon monoxide upon the iron of clay fire bricks, resulting in the reduction of the iron oxide to metallic iron and accompanied by a change in volume, the penetration of carbon resulting from the decomposition of hydrocarbons into the structure and consequent deposition of graphite within the pores, which may bring about the destruction of the refractory, the violent decomposing action of superheated steam, and the absorption of sulphur-trioxide gas. On the other hand, there are certain factors at work which tend to improve the quality such as the volatilization of the alkalies. It has been demonstrated that the latter gradually diminish in amount, with the result that the refractory gains in heat-resisting quality in use, unless, of course, this action is counterbalanced by the absorption of fluxes from ashes, dust, or vapors.

For many purposes products of No. 2 grade are far more suitable than the more expensive high-class refractories.

The best that can be done under the circumstances is to define certain specifications for products required to withstand high temperatures or load conditions at average furnace temperatures—i. e.,

the general high-grade refractory materials. In addition, however, supplementary specifications must be considered in connection with special conditions peculiar to certain industries. The only thing, therefore, that may be attempted at this time is to define high-grade refractories from the standpoint stated, with the definite understanding that such rules can not be applied indiscriminately to all classes of fire-clay materials.

(b) **Expression for Value of a Refractory.**—Baraduc-Muller[61] makes such an attempt by saying that refractories should be purchased according to chemical composition, refractoriness, absolute and apparent density, mechanical resistance to pressure and impact. According to him the value of a refractory would be proportional to the expression:

$$\frac{Al_2O_3}{SiO_2 + \text{fluxes}} + \text{refractoriness} + \frac{\text{absolute density}}{\text{app. density}} + \text{mechanical strength.}$$

(c) **English Specifications.**—A committee of the English Institute of Gas Engineers has proposed the following tentative specifications:[62]

It is understood that this specification applies generally to material made from fire clay containing approximately not more than 75 per cent silica. It is known, however, that there are in certain areas fire clays containing as much as 80 per cent silica, and material made from such clays shall be considered to conform to this specification if it passes the test herein specified.

(1) *Refractoriness.*—Two grades of material are covered by the specification: (*a*) Material which shows no sign of fusion when heated to a temperature of not less than Seger cone 30 (about 1670° C); (*b*) material which shows no sign of fusion when heated to a temperature of not less than Seger cone 26. The test shall be carried out in an oxidizing atmosphere, the temperature of the furnace being increased at the rate of about 50° C per five minutes.

(2) *A Chemical Analysis.*—A complete chemical analysis of the material is to be provided when required.

(3) *Surface and Texture.*—The material shall be evenly burnt throughout and the texture regular, containing no holes or flaws. All surfaces shall be reasonably true and free from flaws or winding.

(4) *Contraction or Expansion.*—A test piece when heated to a temperature of Seger cone 12 for two hours shall not show more than the following linear contraction or expansion: No. 1 grade, 0.75 per cent; No. 2 grade, 1 per cent.

The test piece shall be 5 or 6 cm long, the ends being ground flat and the contraction measured by means of Vernier calipers, reading to 0.1 mm, a suitable mark being made on the test piece so that the calipers may be placed in the same position before and after firing.

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[61] Revue de Metallurgie, 6, No. 6.

[62] The Iron and Coal Trades Review, 92, p. 1041.

(5) *Variation from Measurements.*—In the case of ordinary bricks, 9 by 4½ by 3 inches or 2½ inches thick, there shall not be more than ±1.5 per cent variation in width or thickness, and in all cases the bricks shall work out their own bond, with not more than one-eighth inch allowance for joint. In the case of special bricks, blocks, or tiles there shall not be more than ±2 per cent variation from any of the specified dimensions.

(6) *Crushing Strength.*—The material shall be capable of withstanding a crushing strain of not less than 1,800 pounds per square inch.

(d) **Specifications Based on Results of Load Tests.**—From the results of the work done in this laboratory the following tentative specifications are suggested. In this connection the No. 1 clay refractories are divided into two classes, A and B. The first includes those materials for which both refractoriness and load-carrying ability is required; the second those where refractoriness is demanded but compressive strength at furnace temperatures is not a main requisite. The No. 2 clays are supposed to include those products which are somewhat inferior to the high-grade refractories, but which nevertheless form an important class of products suitable for many uses.

No. 1 A.—Materials of this class should show, when tested in the ordinary manner in the Deville or an electric furnace and heated at a rate so that the final temperature is obtained in not less than one hour, a softening temperature of not less than cone 31, approximately 1690° C.

When subjected to the load test in a manner substantially as described in this bulletin, at 1350° C and under a load of 50 pounds per square inch, a standard fire brick tested on end should show no serious deformation and should not be compressed more than 1 inch, referred to the standard length of 9 inches.[63]

When tested on end, at atmospheric temperature, the compressive strength should not be less than 1000 pounds per square inch.

The product in its manufacture should not be fired to a maximum temperature lower than that corresponding to cone 12, or approximately 1350° C.

Upon chemical analysis the empirical formula calculated from the composition should show a total RO content of not more than 0.22 molecular equivalent, including the iron oxide as FeO.

[63] In more recent specifications the maximum deformation allowed is one-half inch.

No. 1 B.—The average softening point of this class of products should correspond to a temperature of not less than cone 31, about 1690° C.

In the load test it should show no serious deformation or a contraction of more than 1 inch, referred to the standard length of 9 inches, at a temperature of 1350° C and a load of 30 pounds per square inch.

When tested for compressive strength, on end, at atmospheric temperature the crushing strength should not be less than 800 pounds per square inch.

The product should not have been fired to a maximum temperature lower than that represented by cone 10, about 1300° C.

The chemical formula calculated from the analysis should show a content of RO fluxes of not more than 0.22 equivalent.

One important point has been left unconsidered in these specifications, namely, the question of shrinkage or expansion upon heating fire bricks to higher temperatures. It was thought that the data at hand were insufficient to suggest any requirements.

No. 2. Refractories.—The softening point of this class of refractories should not be lower than the temperature corresponding to cone 28, approximately 1630° C.

In the load test the materials of this classification should be able to carry a load of 25 pounds per square inch at 1300° C without serious deformation or a contraction greater than 1 inch, referred to the standard length of 9 inches.

The chemical formula, as calculated from the analysis, should not show a content of more than 0.32 equivalent of fluxes.

It is seen from these requirements that the limits drawn are closer than those generally considered for No. 2 fire clays. However it is believed that with these restrictions this class of refractories would become more generally useful in industrial application.

15. CONCLUSIONS

The load test described in this paper furnishes a criterion of the viscosity of refractories and, therefore, of their load-carrying capacity at furnace temperatures. It has been found that the softening temperature of fire-brick specimens is not a safe criterion

of the "standing-up" quality of fire-clay products. The ability to withstand a load test at 1350° C, with a compression of 50 pounds per square inch, estimates the refractoriness of a material under working conditions. Failure is considered to have taken place when the specimen shows marked deformation or contracts more than 1 inch, referred to the standard length of 9 inches.

It was found that a content of more than 0.22 equivalent of fluxes results in failure in the load test, with a silica content varying up to 1 Al_2O_3 3 SiO_2. With a higher content of silica the permissible RO seems to decrease. Thus with 4.4 molecular equivalents of silica an RO content of 0.17 equivalent may bring about failure.

It has been shown that bond clays of inferior refractoriness can be improved by thorough grinding with flint clay or some other heat-resisting material, low in fluxes.

Refractories should be burned to as high a kiln temperature as possible, at any rate not below cone 10 and better at cone 12.

A good initial compressive strength is desirable for fire bricks subjected to load conditions. When tested on end (at atmospheric temperature) a crushing strength of more than 1000 pounds per square inch is required.

The load test can not be taken as the sole criterion of the value of a refractory, but the softening temperature and the chemical analysis must likewise be considered.

While the load test is important for industrial practice, since conditions of direct and transverse compression and tension exist under nearly all furnace conditions, it is less valuable where the loads imposed are insignificant.

Tentative specifications for No. 1 and No. 2 refractories have been suggested.

WASHINGTON, December 15, 1911.