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OF CLAYS

BY

R. C. PURDY AND J. K. MOORE.

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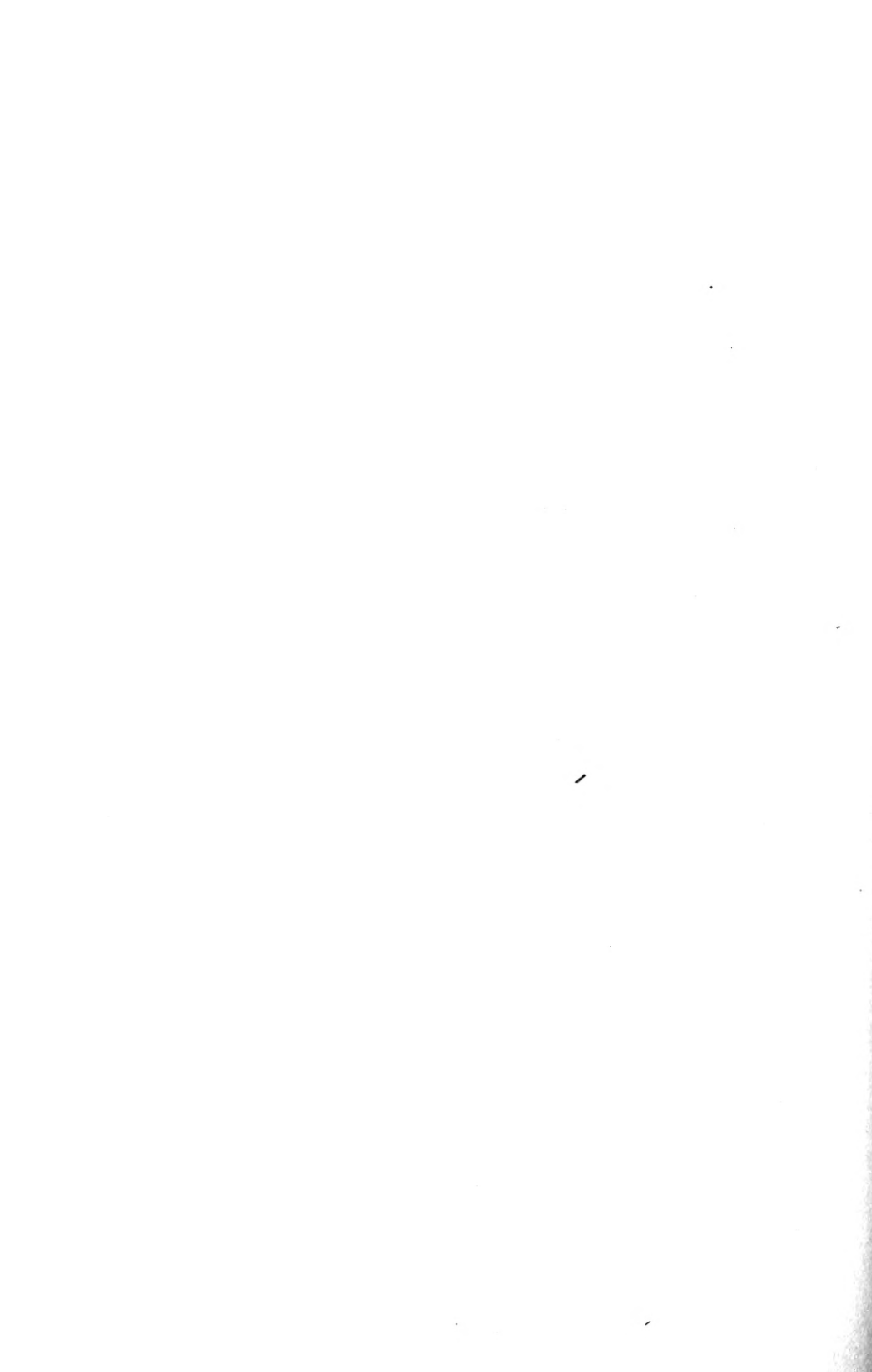
PYRO-CHEMICAL AND PHYSICAL BEHAVIOR OF CLAYS

BY

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INTRODUCTION.

The work of Orton and Griffin on the "Effect of Carbon in the Burning of Clay Wares," Orton on the "Role of Iron in Clays," Kennedy on the "Dehydration of Clay and Decarbonization of Calcium Carbonate," Singer on the "Decarbonization of Ferrous Carbonate," and Lovejoy on the "Expansion of Brick during Water-smoking," etc., are some of the studies of the pyro-chemical and physical behavior of clays that have been reported in the Transactions of the American Ceramic Society. Considerable attention also has been given to similar studies by our contemporaries in the English Ceramic Society during the past three or four years. Time and space will not permit of a review of these studies, nor of the many observations that have been reported in the trade periodicals since ceramics has been classed as a science.

Since in every clay industry it is in the burning that the usefulness of a clay is developed, the burning properties may justly be considered the most essential or vital factors to be studied. A clay may lend itself readily to manufacturing processes, and yet not develop in burning the properties requisite for making it into serviceable ware. Clays may differ widely in chemical, mineralogical, and physical constitution and yet be equally valuable for manufacture into a given product.

In clay burning, the combined influence of the chemical, mineralogical and physical properties of clay constitute the cause, and the pyro-chemical and physical proper-

ties constitute the effects; knowing the causes, the effect ought to be interpretable. Owing, however, to the complex composition of clay and the variable properties of its several constituent parts, the true causes cannot all be ascertained in a sufficiently short time to justify the labor, even if methods were known by which they could be obtained. The effects, however, can be readily observed.

Classification of clays on either the geological or the industrial basis has been attempted by many of the foremost ceramic thinkers, yet it is freely admitted that as yet no satisfactory arrangement has been suggested. There is no agreement between the commercial value of clays and their geological age.

Clays from which first class paving brick can be manufactured, for instance, can be found in strata of any age and under almost any geological condition. Fire clays and shales of all ages are being successfully used in the manufacture of paving brick. Glacial and alluvial deposits of clays have been found that are likewise serviceable for this purpose. Because the chances are far better of finding clays that can be made into paving brick among the fossil clays, the prevalent opinion is that it is to these types that paving brick manufacturers must look for their material. The facts are that there are many shales that are not fit to be manufactured into common building brick, much less into paving brick. Geological age or distribution, therefore, has proven an unsatisfactory basis of classification.

Chemical analyses of clays have been used in some cases as a basis of classification, but so unsatisfactory were the results that but very little importance can be attached to such a classification.

A classification of the clays lying within political or natural boundaries, using as a basis the properties that are most essential to adapt each class to its commercial uses, has been the object of extensive researches of the United States Geological Survey and the various State Geological Surveys. Descriptions of the location and properties of the clays to be found in the several survey re-

ports have failed in this respect. In some Survey reports, notably those of Iowa and West Virginia, a few of the pyro-chemical properties of their clays have been described, but in no case has much significance been attached to their determination. In fact, in no case has the study of the pyro-chemical properties been carried to such a degree of completeness as would warrant very conclusive deductions. Having had opportunity to study the clays of Illinois, under the direction of the Geological Survey of that State, the writers, after nearly three months of research, came to recognize their inability to draw satisfactory conclusions from the several tests made of the properties of raw clays, and to appreciate the importance of a more exhaustive study of the chemical and physical changes that occur during the progress of burning from dehydration and oxidation to fusion.

Believing that a study of the changes in porosity and specific gravity at successively increasing heats affords a practical method for testing and classifying clays, and also a method that makes possible in most cases an accurate estimate of the commercial possibilities of a given class or type of clay, and further being confident that this method makes it possible to determine the most important properties of any clay, we present here a detailed account of the way in which our tests were made and a few of the results of our investigations.

SAMPLES OF CLAY INVESTIGATED.

Location and condition: Clays used by the more important paving brick factories of Ohio, Indiana, Illinois, Missouri, and Kansas were obtained in what was termed "dry-pan samples," i. e. they were taken from the chutes leading to the pug mill, after having been pulverized in the dry pans. Clays collected from several parts of Illinois and not used in the manufacture of ware at the place of sampling, were ground in a five-foot dry-pan in the laboratories of the Ceramic Department of the University of Illinois.

Types: Fire clays, shales and loess were the types of clays tested. There was not a sufficient variety of types nor enough samples of each type on hand to make an exhaustive study, but this lack of samples does not lessen to any great extent the value of the results obtained.

MANUFACTURE OF TEST PIECES.

Wedging: Approximately one pound of dry clay was placed on a dampened plaster-covered table and sufficient water from the city mains added to develop the plasticity required to permit batting the clay into loaves. This was accomplished by adding the water in small quantities, and thoroughly working it into the clay each time, until the mass had the desired plasticity. It was then thoroughly wedged by kneading and batting until, on cutting the mass open, it appeared to be compact, i. e. without air blebs.

Moulding: The loaf was then subdivided into smaller portions, each just sufficient to fill a mould ¾ inch x 2¼ inches x 4¼ inches. The slabs were made to fill the mould by pressure applied in a screw press. They were then placed in a miter-box and cut into brickettes ¾ inch x ¾ inch x 2½ inches.

Marking: The laboratory sample number and a serial number was stamped on each brickette.

Drying: The brickettes were dried in an open room at summer heat. It had been found possible to dry even the most tender of clays in this manner, so it was assumed that all clays used in this test could, without detriment, be subjected to this treatment.

Burning: Twenty-four brickettes of each clay were prepared. The ones on which the serial numbers 1 and 2 had been stamped were placed in a saggar to be drawn at Cone 010, those on which the serial numbers 3 and 4 were stamped were placed in a saggar to be drawn at Cone 08 and so on—each successive pair of brickettes of each clay being placed in a saggar to be drawn at a predetermined heat as follows:

Series No. on brickette	Heat at which drawn	Hours intervening between draws
1, 2	010	Oxidized at 800 for 2 hours. From 800°C to cone 010 6 hours.
3, 4	08	2 hours
5, 6	06	2 hours
7, 8	04	2 hours
9,10	02	2 hours
11,12	1	2 hours
13,14	3	2 hours
15,16	5	2 hours
17,18	7	2 hours
19,20	9	2 hours
21,22	11	2 hours

The brickettes in the saggars to be fired from cones 3 to 11 were packed loosely in coarse white placing-sand, so as to prevent their sticking one to another. Only those clays known to be fire clays, or at least sufficiently refractory to withstand severe heat treatment were placed in the saggars to be drawn at the higher cones.

The eleven saggars were placed in a coke-fired, side-down-draft kiln in a manner convenient for drawing. The "spy" cones were centrally located in the kiln in a shield that protected them at all times from direct contact with the flame. When cone 010 was bent over sufficiently to touch the placque, the wicket was opened enough to draw the cone 010 saggar, the wicket replaced, and the heat slowly raised as shown in the above table.

Cooling: The saggars in which the brickettes were placed were "tile setters" 2 inches deep and 8 inches x 8 inches in area. Before placing another saggar was inverted over the one containing the brickettes, so that on drawing, the brickettes were at no time exposed to the relatively cold temperature of the room, except in one case of accident. The saggars were placed, uncovered, in the ash pit of the kiln, where they were exposed to the direct radiation from the hot grate bars above. In this manner, the brickettes were cooled rapidly at first, thus preventing

the fused portions in the brickettes from crystallizing very much, but from dull redness down to blackness the cooling extended over a considerable period.

The method of cooling pursued in this investigation was not ideal. The brickettes should have been cooled slowly for the first 200°C which, as above stated, was not the case. Inasmuch as there is danger of checking the vitrified brickettes by cooling down to room temperature too rapidly, some attention should be given to the last as well as to the first stage of the cooling period, but more particularly to the first. It was not possible to cool the brickettes under these ideal conditions, for the services of the kiln were in demand for other purposes, and circumstances did not permit of delaying the burning until such times as the kiln would not be in use.

Preparing brickettes for testing: When cooled, sand grains were found to be fused to many of the brickettes, requiring that they be ground off on an emery wheel. Care was taken not to unduly heat the bricks while grinding off the sand, and yet as little water as possible was used. The bricks that were thus ground were washed in distilled water to remove all traces of dirt and adhering particles. From the unground brickettes all adhering particles were removed by a dry stiff brush. Each brickette was carefully examined for flaws induced during manufacture or cooling, and also in order to remove all adhering portions such as broken corners that might have been detached later in the test.

Up to this point, all brickettes were handled together, without regard to sample or series number, except as before indicated.

TESTING OF BRICKETTES.

In all, 60 clays were prepared for testing as above described, using 16 to 22 brickettes for each. The brickettes were now sorted, those of each clay being treated as a unit, so as to insure like conditions at all times for all brickettes of the same clay.

Drying of Brickettes: Brickettes belonging to two or three clays were placed in a drying oven and dried at 240°C. At the expiration of four hours at this temperature, they were cooled in desicators preparatory to obtaining the dry weight of each brickette.

Dry Weights: The dry weight of each brickette was found to the third decimal place on a chemical balance.

Saturation of Brickettes: After the dry weights had been obtained, the brickettes were placed in aluminum pans, keeping them arranged in the pans in their regular serial order.   Distilled water was added until only the upper surface of each test piece was above the level of the water.   This exposure of one face of the brickette was to permit easy escape of the air from the interior of the brick, as it was being displaced by the distilled water.   After standing thus in water for 18 to 24 hours, they were completely immersed.

After a total of 48 hours in water, the brickettes were placed in water under a bell jar, and the air exhausted.   In nearly every case, when a partial vacuum had been created, the air escaped from the brickettes at such a rate and in such volumes as to cause the water to appear to be boiling. From a previous experiment, the data of which are given in the following table, it was thought that in the average case, fairly complete saturation could be attained with 15 minutes treatment in a partial vacuum.

TABLE I.

Showing efficiency of vacuum treatment in affecting saturation.

Sample	Porosity as determined after 48 hrs. saturation without air exhaustion.	Precentage of gain in porosity at conclusion of vacuum treatment extending over period of			
		5 min.	10 min.	15 min.	20 min.
S 2	3.22	48.1	51.8	57.9	65.0
G II	3.3	38.7	42.1	48.4	50.6
K 4b	3.93	27.3	....	35.6	37.5
K 15d	4.22	13.48	14.48	18.7	20.8
K 13c	4.27	44.60	46.60	46.6	46.6
K 15c	4.51	33.40	36.50	36.8	38.2
R 4	5.12	58.2	59.4	61.7	63.7
H II	5.29	31.2	35.4	37.6	38.9
R 2	6.1	27.5	32.2	35.6	36.0
K 6d	6.46	29.9	31.6	35.3	39.3
K 2	6.55	18.6	20.1	21.6	24.3
R 1	6.7	10.2	11.0	11.0	11.0
B II	6.91	28.0	30.4	31.4	32.0
J II	7.53	11.8	13.7	15.7	16.0
I II	8.64	11.8	12.8	14.1	14.8
K 8d	9.06	22.0	23.5	24.0	24.9
B I	9.39	13.11	20.3	23.4	....
K 15b	19.8	6.05	6.22	6.84	7.34

Wet and Suspended Weights: Each saturated brickette was in turn suspended by a silk thread from the beam of a chemical balance, and its saturated weight taken, allowing for the weight of the thread. Without removal from the balance, a glass of water was placed on a bridge spanning the scale pan in such a manner as to cause the brickette to swing absolutely free but completely immersed in the water. The suspended weight of the brickette was thus taken.

Calculations: The percentage of porosity of each brickette was calculated by the formula:

$$\text{Percentage of Porosity} = \left(\frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Wet Weight} - \text{Suspended Weight}} \right) 100$$

This expression for percentage of porosity is, so far as is known to the writers, here first presented. It is a simplified form of the following expression, which is given in

nearly all of the Reports of Geological Surveys on Clays, in which this method of obtaining porosity has been used.

$$\text{Percentage of Porosity} = \left(\frac{[W-D] \text{ Sp. Gr.}}{[W-D] \text{ Sp. Gr.} + D} \right) 100$$

In this latter expression for percentage of porosity, W=wet weight; D=Dry weight. By substituting for the last D in the denominator its value obtained from the expression for specific gravity:

$$\text{Sp. Gr.} = \left(\frac{\text{Dry Weight}}{\text{Dry Weight} - \text{Suspended Weight}} \right)$$
$$\text{or, } D = D \times \text{Sp. Gr.} - S \times \text{Sp. Gr}$$

Where S=Suspended weight, the expression reduces to

$$100 \left(\frac{W \times \text{Sp. Gr.} - D \times \text{Sp. Gr.}}{W \times \text{Sp. Gr.} - D \times \text{Sp. Gr.} + D \times \text{Sp. Gr.} - S \times \text{Sp. Gr}} \right)$$

By canceling "Sp. Gr." and collecting terms, the simplified formula for percentage of porosity first given is deduced.

Plotting of Results: In a previous study of similar character to the one here reported, the writers had arbitrarily established the following proportion: Linear length on ordinate, equal to 1% porosity: linear length on abscissa equal to difference of heat treatment of one cone::1:1. This was maintained between the coordinate factors of the porositygraphs, so that the rate of decrease in porosity could be expressed numerically in terms of the tangency or slope of the curves, and that the factors so obtained would be comparable one with another at all times.

The divisions on the abscissas of the specific gravity curves are the same as those of the porosity curves. The divisions on the ordinate are proportionally; 0.1 Sp. Gr. : 1 cone heat :: 1 : 1.

PYRO-PHYSICAL-CHEMICAL BEHAVIOR OF CLAYS.

The physical-chemical changes that take place in burning may be discussed under three headings:

   1 Water-smoking.
   2 Dehydration and Oxidation.
   3 Fusion.

Water Smoking: During the water-smoking or driving off of the mechanical and hygroscopic water, clay wares expand, as is shown by Mr. Lovejoy's settling curves.[1]

This would scarcely be a noteworthy physical change, were it not for the fact that clays either expand again or retain their expanded form through water smoking to the completion of the oxidation and dehydration period. The writers' experiments have shown that this physical change differs in character and intensity with different clays, but their work is not sufficiently detailed and accurate to formulate data or draw conclusion further than that with some clays this transition period from water-smoking to oxidation is somewhat critical.

Dehydration and Oxidation: The majority of clays are dehydrated completely when subjected to heat at 500°-600°C, others are not. In nearly all fossil clays, dehydration precedes oxidation, while in a few instances the reverse is true, as will be noted later.

It is unnecessary to describe in detail the various chemical changes that occur during this period of the burning, for the alterations in the iron[2] compounds and the oxidation of the carbon[3] have been very exhaustively considered by Orton.

Notable exceptions to the usual behavior during dehydration and oxidation were observed in the study of the Illinois clays:

First. K 14, a mined shale, slaked down to a plastic mass after being subjected to a heat treatment which averaged about 625°C for 16 hours, as shown in the following curve:

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[1]Trans. Am. Cer. Soc. Vol. VII, p 422.
[2]Ibid. Vol. V, p 377.
[3]Second Report, Com. on Tech. Inves., Nat'l Brick Mfg. Assoc.
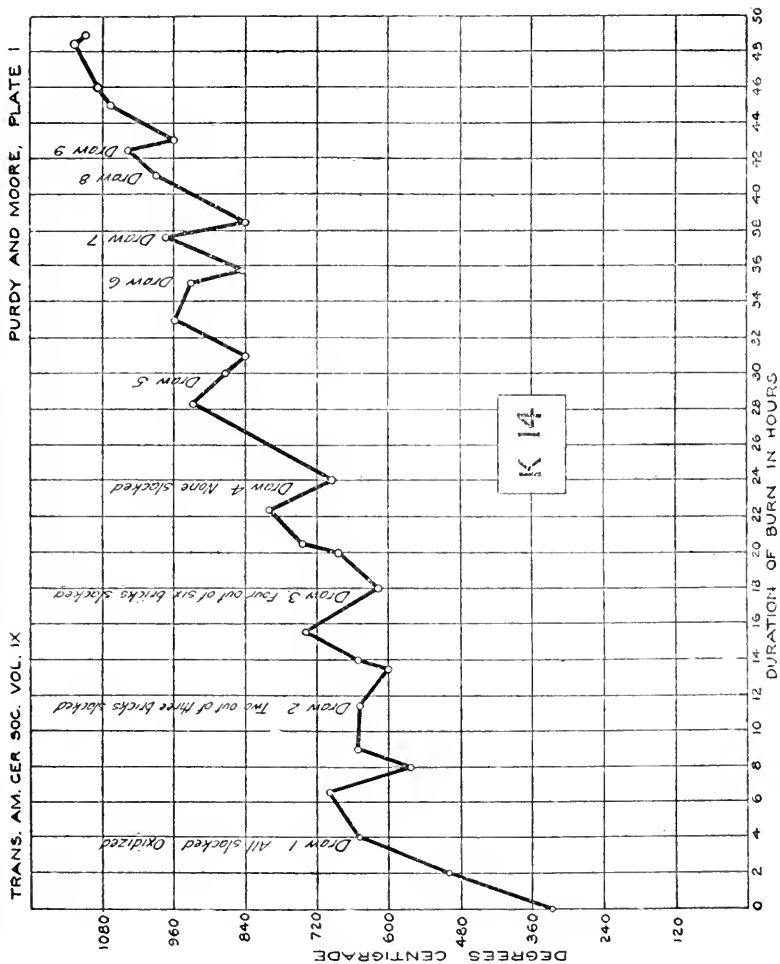
Curve showing the heat-treatment given to clay No. K 14, and the remarkably high temperature required to effect destruction of plasticity.

The shale oxidized easily and before it was completely dehydrated. Six other clays exhibited a reversal of the usual oxidization and dehydration changes, but none in so pronounced a degree as in the case of K 14.

As yet no data have been obtained concerning the chemical or physical constitution of these clays that will shed light upon these rather remarkable exceptions to the usual order in which the dehydration and oxidation take place. The fact is established, however, that the cases are not rare where both changes take place simultaneously, and in a few cases the usual order is reversed.

Second. In the case of H 23, oxidation had not progressed very far at the end of 24 hours exposure at 650°, and the unoxidized portion of the brickettes vitrified on further heating to as hard and dense a mass as did the outer oxidized portions. No swelling or distortion of the brick due to the oxidation of the carbon and ferrous iron was noted. In fact, the shrinkage and rate of decrease in porosity was not abnormal in any respect. In figure 2, are shown the volume-shrinkage, porosity, and specific gravity curves for this clay. (See page 216.)

In this figure, the specific gravity, porosity and volume of the bricks burned at different temperatures are calculated in terms of the percentage of increase or decrease over those of the unburnt bricks. In other words, the raw factors are considered as a basis or datum from which the "burned" factors are calculated as increase or decrease. Zero or the datum line, therefore, represents the data obtained from the unburnt bricks.

The percentage of increase of the burnt ware over that of the unburnt is shown above the datum line on the ordinate, and the percentage of decrease is shown below the datum line. On the abscissae is shown the actual percentage of porosity of the burned brick.

Points on the same ordinate represent a single brick. We have not plotted the data from all the bricks studied in this test, but only those in which the percentage of por-
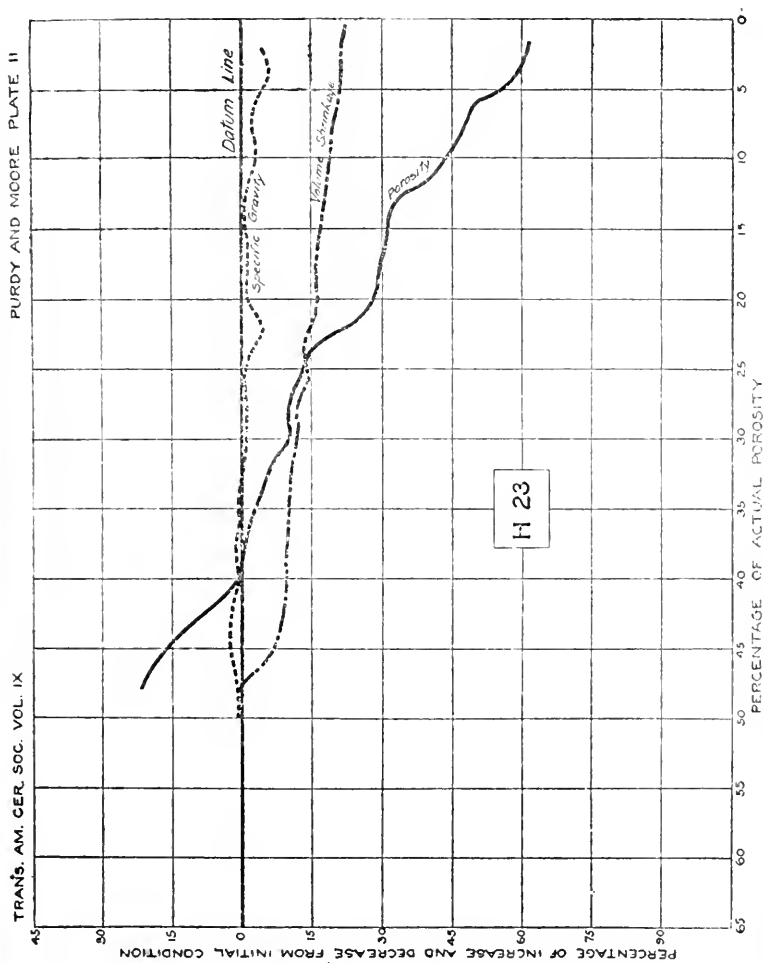
Showing properties of clay H 23, at various stages of burning, compared to its properties in the unburnt condition as a datum.

osity differed sufficiently to fix points on the curves that would show a comparative increase or decrease in the several factors.

The fact that the actual percentage of porosity of the burned brick was taken in each case as a point on the abscissa, without regard to the porosity of the unburnt brick, will account of the irregularity in the curves.

Notwithstanding the fact that the black unoxidized core remained, even when the whole exhibited a porosity of only 2%, the brick continued to shrink normally with each increase of temperature, and the specific gravity of the brick decreased less than in the case of many normally burned paving brick shales. This steady decrease in volume and comparatively slight decrease in specific gravity gives evidence of a thermo-physical behavior that is opposite to that of the majority of clays containing carbon.
(See plate III, facing page 218.)

PHYSICAL CHANGES DURING OXIDATION AND DEHYDRATION.

Contrary to the statements usually made concerning the physical changes in a brick at this period, our investigations show positively that not only the porosity, but also the volume and specific gravity of the brick are increased, and that it is indeed an exceptional case where all of these factors are not larger during the time of oxidation and dehydration than they were in the unburnt condition.

A most peculiar and noteworthy fact in this connection is that in many cases the specific gravity and volume remain large until the porosity has been increased to that of the unburnt brick.

FUSION.

From the laws of physical chemistry, it could not be expected that the heterogeneous mineral mass called clay, consisting largely of amorphous materials, would have a definite fusion point. According to Walker[1], this would more properly be called a fusion period.

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[1] Introduction to Physical Chemistry, p. 64.

Our studies, a part of the data of which are shown in subsequent curves, bear out this statement. It will be seen that in the case of the purest clays, according to the specific gravity curves, fusion begins as early as cone 3. In the case of some of the most impure shales, high in lime, fusion begins at a period considerably earlier than cone 010. Fusion thus early begun progresses with more or less regularity until the whole mass enters into the active thermochemical reaction and deformation of the ware ensues. Incipient vitrification, vitrification, and like terms are only descriptive of the effects at different stages of fusion. It is the rate of fusion, therefore, that determines the pyrophysical effects produced in the burning of clay wares during this period. The factors affecting rate of fusion are:

The factors affecting rate of fusion are:

> 1st. Mineralogical composition.
> 2nd. Size of grain.
> 3rd. Volatile matter.
> 4th. Adsorbed salts.

MINERALOGICAL COMPOSITION.

Synthetical studies of fusions of mixtures of pure minerals, have shown that the same chemical elements, brought together as constituent parts of different minerals, produce mixtures having unlike fusion periods. The rate of fusion and the regularity with which it progresses, as well as the point of complete yielding, are affected very largely by the manner in which the various elements are previously combined. Because of the difficulty of making a microscopic mineralogical analysis of a clay, the knowledge of these facts cannot aid in an attempt to foretell or explain in full the fusing behavior of clays. Realization, therefore, of the fact that difference in mineralogical make-up of clays of like ultimate chemical constitution causes difference in their fusion behavior is the only result of practical value that has so far come from the study of the fusion behavior of synthetical mixtures of minerals.

There is one very notable exception to the above, and that is in the case of calcium carbonate. The effect of calcium carbonate depending upon the size of the grain and extent and homogeneity of diffusion throughout the clay mass, operates in a two-fold manner. If thoroughly blended with the clay in small particles, it operates as a very active flux. Its fluxing effect is most notable on account of the rapidity with which the thermo-chemical reactions between the nascent oxide and clay takes place. This reaction is in some instances so rapid as to make it very dangerous to approach the vitrification temperature. If the calcium carbonate is present in nodules, the thermo-chemical reaction just described can take place only at the points of contact of the decarbonized lime and clay, the remainder of the carbonate being converted into quick lime. The different effects of lime in these two physical conditions on the rate and regularity of fusion of the clay mass is obvious.

SIZE OF GRAIN.

The full significance of this factor can be appreciated only by considering extreme cases, as in the case of calcium carbonate, above cited, or as in a mixture of two minerals such as feldspar and flint. When feldspar and flint are mixed as fine powders in the proportion of 75% feldspar and 25% flint, the mass will be fused to a fluid at approximately 1100°C in a comparatively short time. If, however, these two minerals were placed side by side in the shape of rectangular pieces having the same proportional weight as in the first case, the only fluxing action that would take place at 1100°C would be at the points of contact. Even if the heat was held at 1100°C, complete fusion of the two piecs of mineral could only take place when the glass, formed at the point of contact, enveloped and slowly ate into the unfused portions, and thus produced an intimate mixture of the two minerals by diffusion or surface tension. It is common experience that if complete fusion of the two minerals at 1100°C is desired when brought togeth-
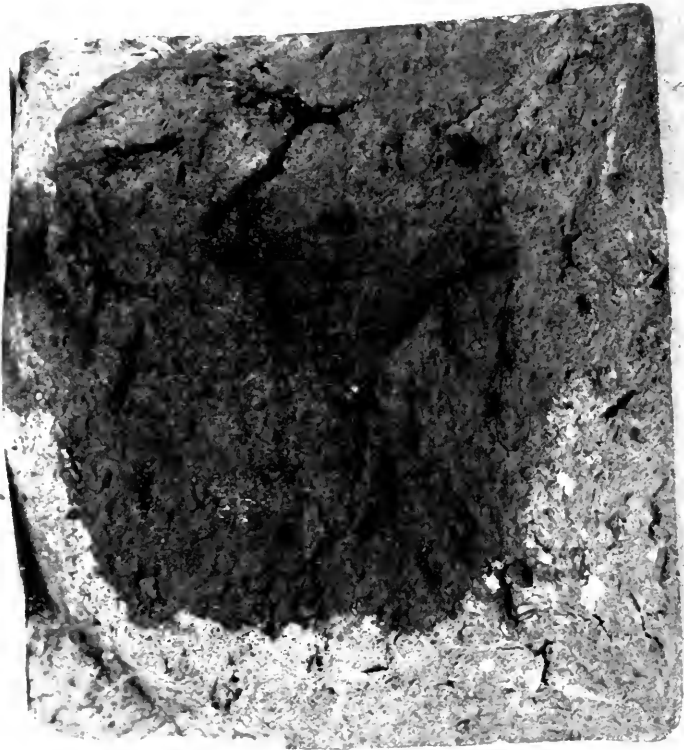
PLATE III. Showing a brick which under-went normal changes in density, specific gravity and shrinkage, in spite of blackening due to imperfect oxydation.

er in the form of coarse particles, considerable time must be
allowed, and that to effect complete fusion in a shorter
time, the heat must be raised from 1100°C to 1230° (ap-
proximately) or the fusing point of feldspar. At this tem-
perature, the feldspar melting would completely envelope
or perhaps float the flint particles, and slowly attack and
dissolve them away, just as water will attack and dissolve
away a piece of loaf sugar.

The above illustration, while an exaggerated case,
nevertheless is descriptive of the effect of fineness of grain
on the fusion of any two minerals that have thermal reac-
tions one with another, and also descriptive of the fusion
of a mixture containing particles of several minerals as a
clay.

In the burning of clay wares, where time is an import-
ant and unavoidable factor, the effect of fineness of grain
influencing the fusing of clays is particularly noteworthy.
By the manufacturers of pyrometric cones it has been re-
cognized as being such a powerful factor that the utmost
care is taken to maintain uniformity in size of grain in
their materials, both before and after manufacture into
powdered cone stock.   The importance of the time factor
has been emphasized in ceramic literature so often as to
render further remarks on this point unnecessary.

VOLATILE MATTER.

Chemically combined water, carbonic acid gas, carbon,
etc., do not of themselves, on expulsion, cause thermo-
chemical reactions to take place between the stable bases,
acids and silicate compounds left behind, but their expul-
sion does involve changes in physical and, in some sense,
chemical conditions that provokes thermo-chemical reac-
tions between the remaining substances. For example, in
terra cotta lumber, sawdust is added, so that when it burns
out, it leaves the mass extremely porous, i. e. not dense as it
would otherwise have been. The sawdust in this instance
has been effective in opening the structure of the ware and

P. & M.—2.

preventing the particles in the clay mass from coming within fluxing distance of one another as they otherwise would. What is true in the case of the sawdust in terra cotta lumber is true of combustible organic matter in clays. It is obvious, however, that the influence of carbon in this connection depends to a very large degree on the size of the carbon particles.

The effect on the thermo-chemical behavior of clays of the expulsion of CO_2 from such compounds as ferrous carbonate, calcium carbonate, etc., is another familiar phenomenon, the importance of which is not recognized in the attempt to interpret the results of an ultimate chemical analysis. If two equal portions of the same clay are taken, and to the one a quantity of red iron oxide (Fe_2O_3) and to the other an equivalent quantity of powdered ferrous carbonate ($Fe\,CO_3$) and the two mixtures burned under the same thermal conditions, it will be found that the mixture containing the ferrous carbonate will begin to fuse earlier, exhibit a more erratic rate of decrease in specific gravity as the intensity of the heat increases, and may or may not, depending upon conditions other than those here considered, cause an earlier ultimate fusion. The same is true to a greater or less extent in the relative fluxing effect of the oxides and carbonates of other bases.

The same phenomena are also notable in the comparative fluxing effect of such hydrous and anhydrous silicate compounds as raw and calcined kaolin.

When one ingredient of a chemical compound is driven out by heat, or otherwise separated, the remaining portion is said to be in the nascent state, i. e. eager to combine with anything for which it has an affinity. If in an intimate mixture of clay and calcium carbonate, the clay is being dehydrated at the time the calcium carbonate is losing its CO_2, rapid fluxing between the two will ensue. In fact, dehydration of clay in the presence of calcium carbonate causes earlier expulsion of the carbonic acid gas from the carbonate.

ADSORBED SALTS.

The influence of the adsorbed salts in a clay on its pyro-chemical and physical changes are not very well understood. In fact, little is known about adsorbed salts beyond the fact that they are present in nearly all, if not all, plastic clays. A few thermal phenomena, however, are unexplainable except on the assumption that adsorbed salts are present in such forms and quantities that they may be considered as the cause of these phenomena.

In the first place, assuming that it is the influence of adsorbed salts that gives to a clay its plasticity, (an exceedingly probable assumption) the peculiar fact that sample K 14, before cited, could retain considerable plasticity even after subjection to a temperature of 625°C for 16 hours may be explained by the possibility that some of the adsorbed salts had either not lost their peculiar properties of giving to the clay grains a slipperiness which we call plasticity, or that they regained these properties by rehydration. The same may be said in regard to the plasticity developed in slate and hornblend by wet grinding.

Further, the adsorbed salts may be volatilized at temperatures that are sufficient to cause the dehydration of clays. We know that considerable material can be volatilized from clay by dry distillation, and it seems safe to assume that the material so volatilized was present in the clay as salts unstable at comparatively low temperatures. Hopwood[1] has shown that the volatile material may possibly in some cases be silica or alumina. Dr. Kahlenburg in a lecture delivered at the University of Illinois reported the finding of a surprisingly large quantity of SiO_2 in the gases given off from fodder in Silos. In fact, sufficient evidence is at hand to warrant the assumption that the adsorbed salts of a clay may be of various composition, and need not necessarily be alkaline salts. Loss of plasticity due to the volatilization of the soluble salts before they have had opportunity to operate as fluxes therefore, is a

[1]Trans. Eng. Cer. Soc., 1904-5, p. 37.

very probable fact. It is equally probable that there are
some adsorbed salts which either are not volatile, or are
so confined in the clay that they are not expelled on
heating.

If any salt is thus retained on heating, the clay can
readily slake down in water to a mass, the plasticity of
which is proportional to the amount of retained soluble salt
and degree of delinquesence of the salt so retained. It is
not uncommon to find soft burned brick and drain tile
slaking down to a plastic mass.

It is a fact, also, that the least plastic clays and conse-
quently, according to the cause of plasticity assumed in
these discussions, those containing the least amount of
adsorbed salts, require higher heat to make a sound frost-
resisting ware, and that in most cases the clays that can be
burned into such ware at the lowest heats are very plastic.
In the first of the cases, there is an absence of a fluxing
medium between the grains and in the second case the salts
at their melting heat fuse and cement the grains.

If, however, all the salts have neither been volatilized
nor fused, it may be that they are retained in a loose com-
bination with the dehydrated silicate of alumina, which
can be broken down under the influence of water, and both
the salt and kaolin rehydrated. This assumption is believed
to be substantiated by the fact that it was the brick made
from clays whose so-called coarse grains were not indivi-
dual crystals, but bunches of minute grains cemented to-
gether by a salt that is but slightly soluble and hence re-
sists disintegration in water even under long and severe
treatment, that slaked after having been subjected to 625°C
in the kiln.

PRECIPITATED MATERIAL.

Calcium carbonate, hydrates of silica, alumina, and
iron, as well as zeolitic compounds, when first precipitated
or formed, are in the majority of cases in extremely fine
grains. The fluxing behavior of any substance is mater-
ially different when thoroughly disseminated in minute

grains, especially in the colloidal form, than when present in coarser grains.   Iron, for instance, has been found to enter into chemical combination with silica as a ferric silicate when the iron is precipitated on flint and as a ferrous silicate, if at all, when the two are mixed as dry powders.[1] The vast·difference between the fluxing action of ferrous and ferric oxides and compounds need not be discussed at this time.   The important fact in this connection, however, is that it depends to a very large extent on the form and manner in which the iron is disseminated through the clay, as to whether it will combine as the lower or higher oxide. What is true of iron in this regard is true in a degree of other fluxes.

SUMMARY OF FACTORS AFFECTING MANNER OF FUSION OF CLAYS.

1st.   The manner in which the several constituent elements are combined, one with another, very materially affects the fluxing behavior of a clay.

2nd.   The size of grains of the several mineral constituents is an important factor in determining the fusing behavior of clays.

3d.   The amount, form, and character of the volatile constituents of clay does not directly affect the thermochemical reactions, but the difference in the physical condition, structure of the clay, and the stability of the nonvolatilized compounds caused by the expulsion of these substances, does materially affect the manner in which fusion takes place.

4th.   The importance of the role that adsorbed salts play in the fusing behavior of clays is little appreciated. The evidence on the manner in which they operate is so indirect and circumstantial that definite statements or conclusions are impossible.   That they are important factors, however, there is no doubt.

5th.   Concerning precipitated materials, we have evidence from synthetical experiments that prove beyond a

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[1]Trans. Am. Cer. Society, Vol. VII.

doubt that they must be considered as most potent in affecting the fusion of clays.

From the above remarks, it is evident that the writers have but little confidence in the efficacy of an ultimate analysis of a clay as a means of foretelling its burning properties. The combination, size of grain of the several compounds, solubility, volatility, and dissemination of the several salts, and lastly the manner in which the uncombined oxides are introduced into the clay are omre effective factors that the total ultimate composition.

THERMO-CHEMICAL AND PHYSICAL CHANGES DURING FUSION.

It is indeed very difficult if not impossible to determine what the actual thermo-chemical reactions really are, which take place in the fusion of the clay particles first between themselves, and secondly when the whole mass becomes a more or less homogeneous glass.[1] By the aid of the microscope, as will be seen later, more can be told in this respect than by any other means. But the effect of thermo-chemical reactions, however, can be detected by the changes in porosity and specific gravity. Because of our present inability to ascertain in full the reactions that take place, it seems best to refer to the chemical phases of fusion as "changes" instead of "reactions."

The greater portion of the constituents of our clays being mineral substances, many of which do not entirely lose their identity in the burning of clay wares, it is most natural that these should exhibit in nature the same changes when treated separately that they do when heated together in clays. Roth[2] gives the following description of the physical changes in minerals on melting:

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[1] Prof. G. Tamman, Sprechsaal No. 35, 1904, summarizing his studies on silicates says, "The volume of the glass is, at the lowest temperatures, larger than that of crystals." Mellor, Vol. V, p. 78, discusses the volume changes in silicates and cites A. Laurent (Ann. Chim. Phys. (2) 66, 96, 1837; A. Brongniart, Traite des Arts Ceramiques, 1, 283, 720, 1877) and G. Rose (Pogg., 111, 123, 1890; A. S. Day and E. S. Sheperd, Am. Journ. Science, (4) 22, 262, 1906. Dr. E. Berdel (cited Vol. VII, p. 148 A. C. S. Trans.) describes similar physical changes in the heating of ceramic materials and bodies.

[2] Allgemeine und Chemische Geologie, Vol II, p. 52.

Mineral	Specific Gravity of the Crystal	Spec. Grav. when melted to Glass	Percent. Reduct'n in Spec. Grav.	Remarks
Quartz	2.663	2.228	16.3	
Quartz	2.65	2.19	17.3	Average
Olivine	3.3813	2.8571	15.6	
Mica	3.0719	2.2405	27.0	Glass compact
Adular	2.561	2.3512	8.1	
Adular	2.5522	2.33551	8.5	Glass full of fine bubbles
Sanidine	2.58	2.381	7.6	Glass full of fine bubbles and dark-colored.
Orthoclase	2.574	2.328	9.6	Glass full of fine bubbles
Orthoclase	2.5883	2.3073	10.9	Glass colorless
Microcline	2.5393	2.3069	9.1	Glass colorless
Albite	2.604	2.041	21.6	Full of fine bubbles; white glass
Oligoclase	2.66	2.258	15.1	Glass full of fine bubbles
Oligoclase	2.6061	2.3621	9.1	White glass; bubbly
Oligoclase	2.6141	2.1765	16.7	Glass full of bubbles
Labradorite	2.7333	2.5673	6.1	Glass slightly bubbly, with black and white portions
Hornblende	3.2159	2.8256	12.2	Glass compact
Augite	3.2667	2.8035	14.2	Glass compact
Epidote	3.409	2.984	12.5	
Red brown garnet..	3.90	3.05	20.5	Green glass
Lime-iron garnet ..	3.838	3.340	25.6	
Granite	2.680	2.427	12.9	Green Glass; transparent strongly blebbed.
Granite	2.751	2.496	9.3	Black Glass; opaque; strongly blebbed.
Hornblende granite	2.643	2.478	6.2	Black Glass; opaque; strongly blebbed.
Felsite porphyry...	2.576	2.301	10.7	Transparent very blebby difficult of fusion.
Syenite	2.710	2.43	10.3	Glass homogeneous; dark colored.
Quartz diorite	2.667	2.403	9.8	Glass homogeneous; dark colored.
Diorite, quartz free	2.779	2.608	6.3	Black Glass; opaque; compact; somewhat difficult to fuse.
Gabbro	3.100	2.664	14.2	Black opaque glass; easily fusible.

The alterations in the minerals and rocks above cited are those induced when they are changed by melting, from a crystalline to an amorphous condition.   Such complete changes as this cannot be permitted to take place in the burning of clay ware, and yet, as will be shown, the percentage of decrease in specific gravity of many of our clays from the unburnt to the vitreous stage is greater than that given in the above data.   This being true, it is evident that there are factors other than the alteration of minerals from the crystalline to the amorphous condition that affect decrease in the specific gravity of clays.

In the following table are given data which show the effect of heat on physical structure of brickettes made from various clays:

Type of Clay	Sample No.	Normal Vitrification			Maximum Heat Treatment			Rattler Loss on Commercial Product	Remarks on Condition at Maximum Heat Treatment.
		Cone No.	% decrease in Sp. Gr.	Porosity	Cone No.	% decrease in Sp. Gr.	Porosity		
No. 1 Fire Clay	H 24	..	....	....	9	5.38	20.9	....	Light buff. Black iron specks.
No. 1 Fire Clay	V 11	..	....	....	9	5.6	20.2	....	Flashed. Small black iron specks.
No. 1 Fire Clay	F 5	..	....	....	11	4.7	16.6	....	Light buff. No iron specks.
No. 1 Fire Clay	F 19	..	....	....	11	4.1	17.9	....	Dark buff. No iron specks.
No. 1 Fire Clay	F 18	..	....	....	11	5.2	14.1	....	Flashed. Small black iron specks.
No. 2 Fire Clay	V 4	..	....	....	11	4.2	10.65	....	Bluestoned. No black iron specks. Coarse grains.
No. 2 Fire Clay	F 4	..	....	....	11	8.8	11.3	....	Flashed. No iron specks.
No. 2 Fire Clay	F 21	..	....	....	9	7.66	11.7	....	Bluestoned. No iron specks.
No. 3 Fire Clay	R 1	5	3.14	10.2	11	8.66	4.26	16.92	Bluestoned. No iron specks.
No. 3 Fire Clay	V 5	7	8.5	9.19	11	8.6	3.46	....	Heavily flashed. No iron specks.
No. 3 Fire Clay	F 20	5	14.5	10.9	11	17.3	3.36	....	Bluestoned. Even color. No swelling apparent.
No. 3 Fire Clay	F 7	5	7.3	5.01	11	11.9	5.7	....	Bluestoned. Black iron specks very pronounced.
No. 3 Fire Clay	K 12	3	4.16	9.35	9	16.2	3.47	....	Bluestoned. Local patches of glass. No swelling.
No. 3 Fire Clay	V 3	5	4.3	13.35	11	10.6	4.20	....	Bluestoned. Large black iron specks.
Paving Brick Shales	K 1	5	15.0	7.4	9	36.0	2.2	15.82	Dark red at cone 3, swollen & self-glazed at cone 9
Paving Brick Shales	K 2	3	6.7	4.6	5	19.7	....	17.48	Bright red at cone 1, chocolate at cone 3 and black at cone 5. No apparent swelling at cone 5
Paving Brick Shales	K 3	5	10.7	6.9	9	29.6	2.4	24.89	Chocolate in color at cone 5, black at cone 7 and 9. Swelling began at 7
Paving Brick Shales	K 4	5	12.7	3.9	9	29.5	3.7	19.11	Dark red at cone 3, black at cones 5, 7 and 9. Swollen quite badly at 9
Paving Brick Shales	K 6	3	8.1	7.4	9	30.0	3.0	13.25	Dark red at cone 3, spongey at 9 and black in color
Paving Brick Shales	K 8	5	17.7	13.3	9	19.6	5.4	20.25	Same as K6
Paving Brick Shales	K 11	3	7.7	11.9	7	23.0	5.2	28.13	Black but not swollen at cone 7

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Type of Clay	Sample No.	Normal Vitrification			Maximum Heat Treatm't			Rattler Loss on Commercial Product	Remarks on Conditions at Maximum Heat Treatment
		Cone No.	% decrease in Sp Gr	Porosity	Cone No.	% decrease in Sp. Gr.	Porosity		
Paving Brick Shale	K 14	5	13.6	7.0	7	19.00	3.3	21.24	Red at cone 3, dark at cone 5 and Black at cone 7. No swelling apparent.
Paving Brick Shale	R 2	3	5.57	11.0	11	26.00	1.4	17.80	Bright red at cone 3. Swollen and self-glazed at 11
Paving Brick Shale	B II	3	8.1	14.4	9	33.00	4.1	28.05	Darkened at cone 3, self glazed at 5, swollen at 9
Paving Brick Shale	G II	3	10.6	7.17	.	....	....	12.76	Bright red at cone 1, dark red at 8, self-glazed at 5, Swollen at 9
Paving Brick Shale	L 11	5	7.86	1.74	9	23.0	1.97	18.58	Dark red at 3, self-glazed at 5, not swollen at 7
Paving Brick Shale	J II	5	9.72	5.32	7	14.3	1.62	17.14	Dark red at 3, quite spongey at 9, black at 7
Paving Brick Shale	V 9	3	13.1	14.5	9	35.1	3.4	....	Dark red at 3, self-glazed at 7, local glass patches at 9, with but very little swelling
Paving Brick Shale	V 7	5	11.2	8.2	9	21.5	2.9	....	Dark red at 3, self-glazed but not swollen at 5
Paving Brick Shale	F 1	5	17.7	6.5	.	....	....	20.84	Chocolate at 3, self-glazed at 5, swollen at 7
Building Brick Shale	H 16	3	6.15	7.85	9	30.77	2.1	....	Began to swell at cone 1
Building Brick Shale	H 17	1	9.09	7.50	3	39.3	6.0	....	Cone 5 brickettes missing
Building Brick Shale	H 21	3	15.8	7.0	.	....	....	....	Cone 5 brickettes missing
Building Brick Shale	S 1	3	7.2	13.6	.	....	....	26.23	Swollen at cone 5
Building Brick Shale	V 6	3	19.0	7.95	5	42.00	5.6	....	Cone 5 brickettes missing
Building Brick Shale	V 1	3	8.8	8.37	.	....	....	....	Olive green at cone 5, began to swell at 7
Building Brick Shale	V 10	5	10.8	2.25	11	33.0	1.6	....	Bright red at cone 06, chocolate in color and began to swell at 04, swollen irregularly at 1
Building Brick Shale	F 8	04	14.8	6.66	1	22.8	2.87	....	Bright red at cone 02, dark red at 1, self-glazed and badly swollen
Building Brick Shale	F 9	02	6.0	10.04	1	49.7	6.6	....	Bright red at cone 06, bright red at 04 but badly swollen, still red at cone 1
Building Brick Shale	F 10	06	7.84	6.42	1	51.0	8.86	....	
Building Brick Shale	V 2	1	1.5	1.64	9	24.0	4.56	....	Did not bloat materially at cone 9

It was a surprise to learn that bricks will decrease in volume without loss of weight, and at the same time decrease in specific gravity. Had the clay been carried to complete fusion, i. e. to a glass, the decrease in specific gravity would have been credited to the same phenomenon as in the case of minerals, i. e. the changing of its constituents from crystalline to amorphous forms. But in the case of a clay brickette, a very small portion of which consists of crystalline substances, decreasing in specific gravity before the minerals have been rendered amorphous, i. e. fused to a glass or even before vitrification has been completed, can not be explained wholly on this basis. Mr. Wegemann, of the Geological Department was, therefore, requested to make a microscopic study of brickettes of two different clays burned at different temperatures, and his report follows:

NOTES ON THE MICROSCOPIC STRUCTURE OF CERTAIN PAVING BRICK CLAYS, AT VARIOUS STAGES OF FUSION.

In the hope of explaining some of the phenomena of simultaneous decrease in volume, porosity and specific gravity without loss in weight, and to obtain some idea of the manner in which fusion takes place in a vitrifying brick, microscopic sections were prepared from brickettes of two paving brick clays manufactured and burned by Messrs Purdy and Moore in the manner described by them.

Thin sections of brickettes burned at a low temperature exhibit under the microscope a very fine-grained fragmental ground mass, or matrix, in which are imbedded crystalline and other fragments, which were present in the original clay. From these materials are developed at high temperatures amorphous glass and crystals.

The cavities between the particles of a brick may be divided into two classes:

(1) Pores, which are present in pieces fired at low temperatures, due to the incomplete consolidation of the clay. These are the original interstitial spaces of the unburnt clay.

(2) Blebs or bubbles, which are formed in the glass at higher temperatures by the liberation and expansion of gases.

Pores of the first sort are of small size and irregular outline. As the temperature increases, and the material of the matrix gradually fuses into glass, these interstitial spaces tend to disappear.

Cavities of the second sort, which we may for convenience designate as blebs, are simply gas bubbles in glass. They are circular in outline and vary greatly in size. They are not present in the bricks burned at lower temperatures, but appear only after the formation of considerable glass.

DESCRIPTION OF SLIDES.

The R 3 Series. R 3—14. This brickette was drawn at cone 3, or about 1190°C. The color is red. Under the

microscope, the earthy matrix or ground mass is dark brown, the color being due to the presence of iron oxides.

The mineral fragments are quartz, feldspar and mica, named in the order of their abundance. They are angular in outline; the thin edges being sharply defined.

Glass has formed to some extent throughout the ground mass, and in a few instances it has separated out into clear transparent masses, in several of which blebs appear. The blebs, however, are so few and so small that the cavities may be considered as made up almost entirely of pores of the first class. As estimated under the microscope, the porosity is 1.9%.

R 3—16.   Drawn at cone 5, or approximately 1230°C; color dark brown. Under the microscope the ground mass appears somewhat denser and darker than in R 3—14. The quartz fragments are apparently unchanged. The feldspar fragments, however, have disappeared.[1] Mica is present, but in very small quantity.

Glass has been formed in considerable amount. It appears in clear transparent areas, aften 0.1 M.M. in diameter. In some of the glass, needle-like crystals have begun to form, but where free from these the glass is colorless. This fact would seem to indicate that but little iron has entered into its composition.

As stated above, fine needle-like crystals are often present, imbedded in the glass. They do not appear to have any definite arrangement with respect to each other, but occur singly or in dense masses. When viewed singly they are colorless, but when seen in masses, they possess a greenish yellow tint, which they impart to the glass in which they are imbedded. What the crystals are was not determined.

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[1] Hintze gives the fusion points of the feldspar as ranging from 1140° C. in sanidine to 1230 C. in labradorite. In the brickette under consideration it is evident that the feldspar has fused into glass. It is to be supposed that in this fusing, it would flux some of the quartz. If it did so, however, the quartz must have been furnished by the ground mass, for the coarser fragments are apparently not changed in outline nor diminished in amount.

The iron oxides present in the matrix have become segregated into dense masses, which, where they transmit light at all, show the red of hematite, but no definite crystals are to be seen. Pores of the first class have disappeared, and blebs in the glass have become numerous and large, their average diameter being 0.066 m.m. The estimated pore space has increased to 4.2%.

R 3—18. Drawn at cone 7, or 1270°C. The fragments of quartz appear unchanged. The earthy ground mass is rapidly fusing into glass, which has increased greatly in amount over that in the preceding slide. The fine needle-like crystals are also present in greater number.

Minute crystals of iron oxide are seen, apparently in the form of rhombohedrons, having slightly concave faces. They do not exceed 0.0014 m.m. in diameter. The blebs have an average diameter of 0.1 m.m. and the pore space has increased to 12.0%.

R 3—20. Drawn at cone 9, or approximately 1310°C. Quartz fragments are present as before, but occasionally one is observed the edge of which have fused into a glass. The needle-like crystals are everywhere present in the glass, giving to it the yellowish-green tint before mentioned. The iron oxides appear much the same as in the last specimen. The blebs are but little changed.

R 3—22. Drawn at cone 11, or approximately 1350°C. The earthy matrix has given place entirely to glass.

Quartz fragments are still present, but thin; their edges have been rounded by fusion.

The fine needle-like crystals in the glass have increased greatly in length, being in some cases 0.03 m.m. long. They exhibit for the first time a marked tendency to collect in radiating clusters. Often they appear to be attached to the corners of the crystals of iron oxide. These latter have increased in number and size, being 0.005 m.m. in diameter. In some cases the individuals unite, forming long serrated columns.

Blebs have increased greatly in size, their average diameter being 0.128 m.m. The pore space as estimated from them is 19%.

The G II Series. G II—10. Drawn at cone 02, or approximately 1110°C. Color, brick red.

As in the series already described, the mineral fragments consist of quartz, feldspar and mica. Very little glass seems to have developed at this temperature, and no blebs are present. The pore space is made up entirely of pores of the first class, or those due to the imperfect consolidation of the bricks. The average diameter of these pores is 0.065 m.m., and the pore space as calculated is 2.6%.

G II—12. Drawn at cone 1, or approximately 1150°C. Color red.

A little glass appears, but no blebs are seen. The average size of pores is lower than in the last slide, being 0.045, but the pore space as estimated runs a little higher, or 3.6%.

It may be remarked that in the slides studied there is no marked increase in the pore space, as temperature increases, up to the point where blebs appear. From that point on, pore space increases rapidly.

G II—14. Drawn at cone 3, or approximately 1190°C. Color, reddish brown.

Fine needle-like crystals have formed in the glass. A few blebs appear, but are not in sufficient number to affect the pore space materially. As estimated it is 3.2% while the average size of the pores of both classes is 0.06 m.m.

G II—15. Drawn at cone 5, or approximately 1230°C. Color, dark brown.

Quartz fragments are still present, but the feldspar and mica have disappeared. Glass has formed in great quantity, being colorless, or when acicular crystals are present, greenish yellow. These crystals are present in great numbers and resemble those described in the former series. Microlites of iron oxide are also present, but have not yet grouped themselves in dendritic forms. Pores other than

blebs have disappeared, but the blebs have increased greatly in size, the average diameter being 0.175 m.m. while the pore space amounts to 12%.

Generalized Summary of Changes observed at different Heat Treatments.

Cone 02.—Quartz and feldspar fragments are unchanged.
    But little glass is developed.
    No blebs have yet formed.
Cone   1.—No marked change has taken place over cone 02.
Cone   3.—A small amount of glass is developed from the ground mass.
    A few blebs appear.
    Needle-like crystals are developed in the glass.
Cone   5.—Feldspar fragments are fused into glass.
    Quartz fragments are unchanged.
    Blebs increase in number and size.
    Minute crystals of iron oxide develop.
Cone   7.—Glass increases in amount.
    Blebs increase in number and size.
    Quartz fragments are unchanged.
Cone   9.—Quartz fragments begin to fuse into glass along their edges.
Cone 11.—Ground mass is completely fused into glass.
    Some rounded quartz fragments still remain.
    Blebs have increased remarkably in size and number.
    Microlites are more numerous.

It should be borne in mind that this is but a preliminary study. The number of slides examined is too limited to warrant broad generalizations.

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Owing to the absence of similar data on other clay samples and the incompleteness of the present researches, the writers have no definite conclusions to present con-

cerning the surprising facts presented by Mr. Wegemann. This data does, however, establish the facts that neither a mineralogical analysis nor an ultimate or rational analysis of clay will give indication of the nature of its pyro-chemical and physical behavior. Indeed, the above data would seem to throw doubt on the value of a pyro-chemical and physical study of a synthetical mixture of minerals as a basis on which to interpret the thermal changes in an "unknown" clay mixture.

In the following curves, plates IV and V, are shown the specific gravity, volume shrinkage and changes in porosity in the two clays of which microscopic studies were made by Mr. Wegemann. It will be seen that all three factors decrease simultaneously, showing that the increase in bleb structure is not sufficient to counteract the shrinkage of the mass as a whole, and is not to be accounted for by the sealing up of the original pores.

If the minerals and the iron do not enter into the thermo-chemical reactions, as has been heretofore supposed, and if the thermo-physical changes are dependent entirely upon the chemical changes, it is at once obvious that the potency of the influence of size of grain, adsorbed and precipitated substances, has been demonstrated.

CLASSIFICATION OF CLAYS.

On the basis of the characteristic differences in their pyro-chemical behavior, a few of the clays tested in this investigation have been grouped into types as follows:

1. No. 1 Fire clays.
2. No. 2 Fire clays.
3. No. 3 Fire clays.
4. Paving brick shales.
5. Building brick shales.

Further differentiation of these clays is possible; for instance, clays exhibiting change in porosity with successively increasing heat treatment similar to that of V. 2, shown in the following curves, may be classed as sewer and side walk brick clays. (See porosity and sp. gr. curves for V. 2).

& M.–3.
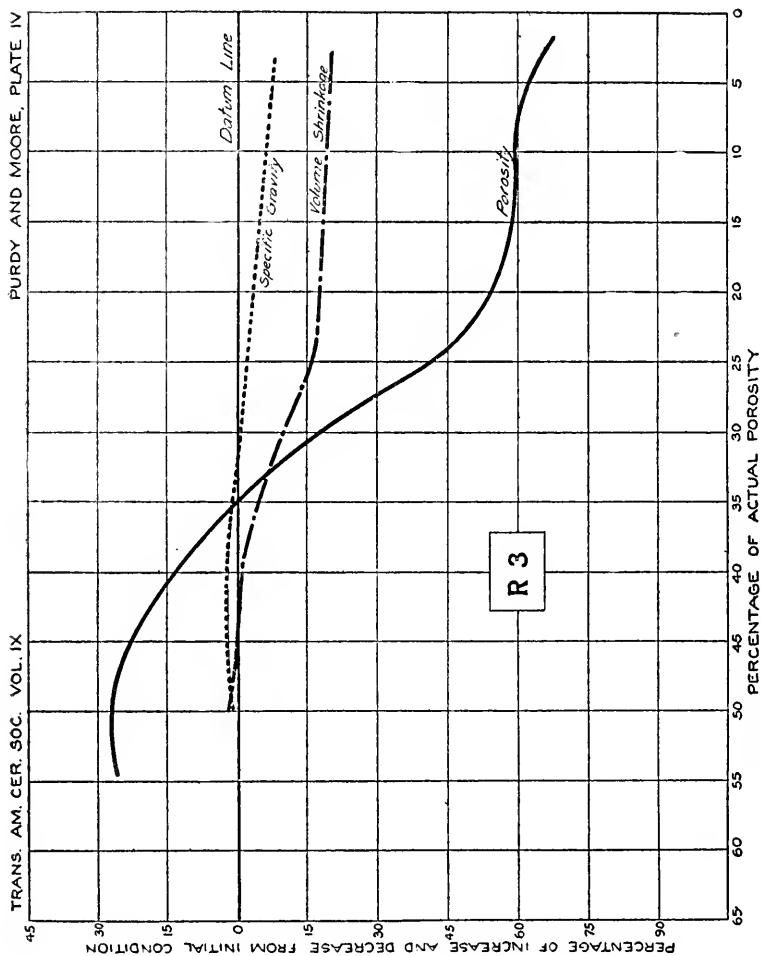
Showing properties of clay No. R 3, at various stages of burning, compared to its properties in the unburnt condition as a datum.
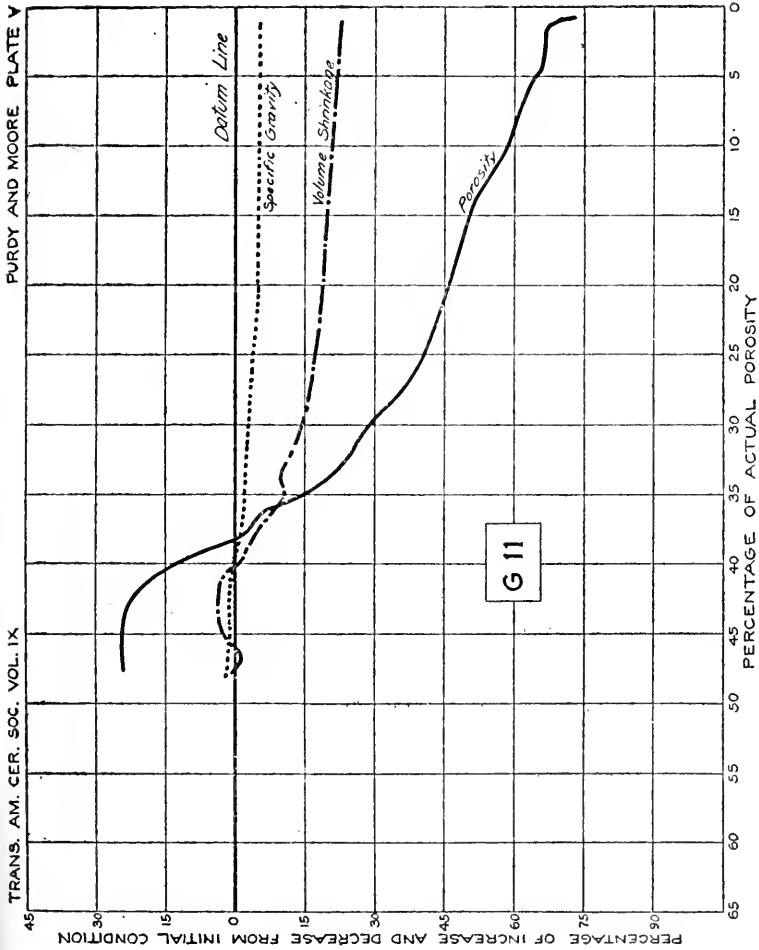
Showing properties of clay No. G 11, at various stages of burning, compared to its properties in the unburnt condition as a datum.
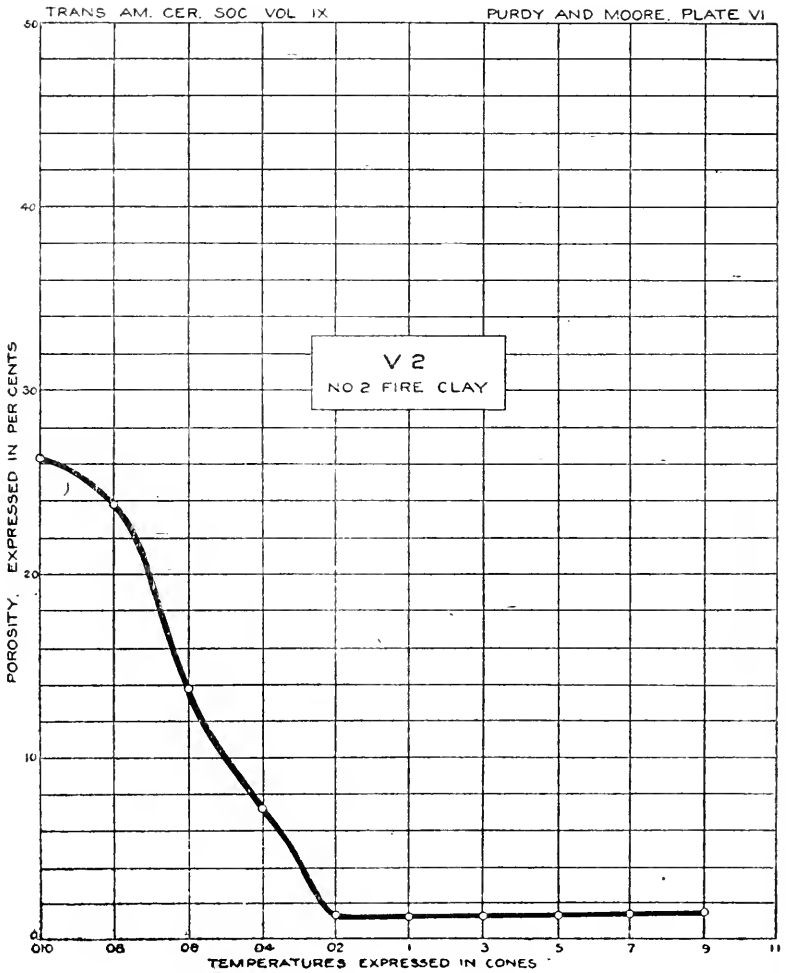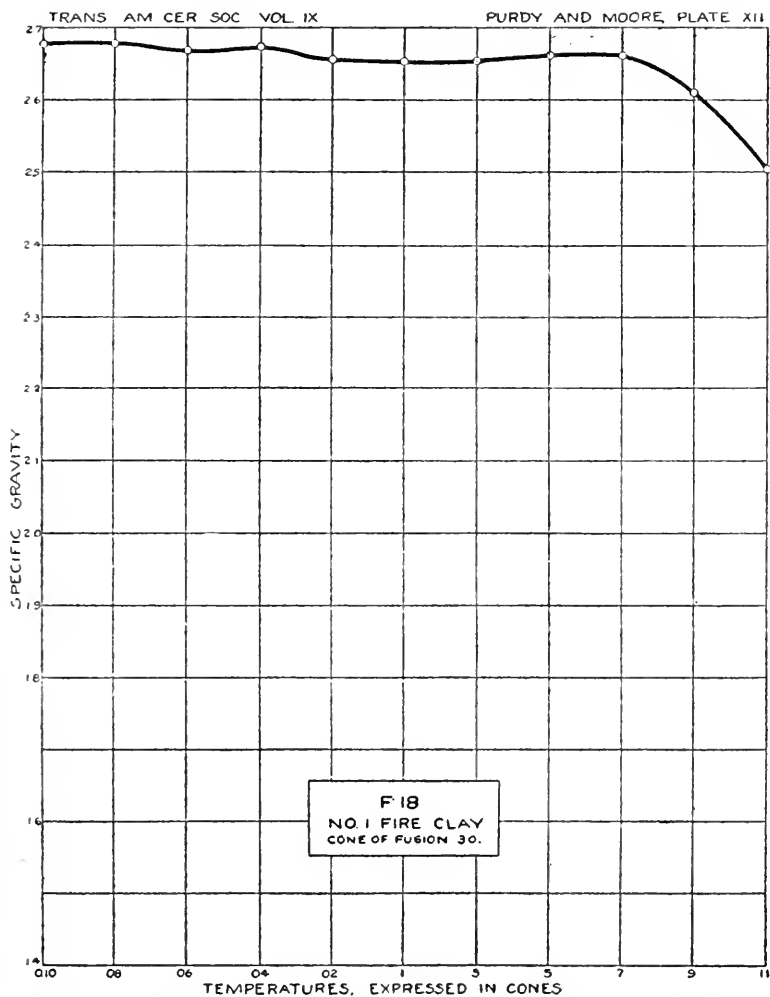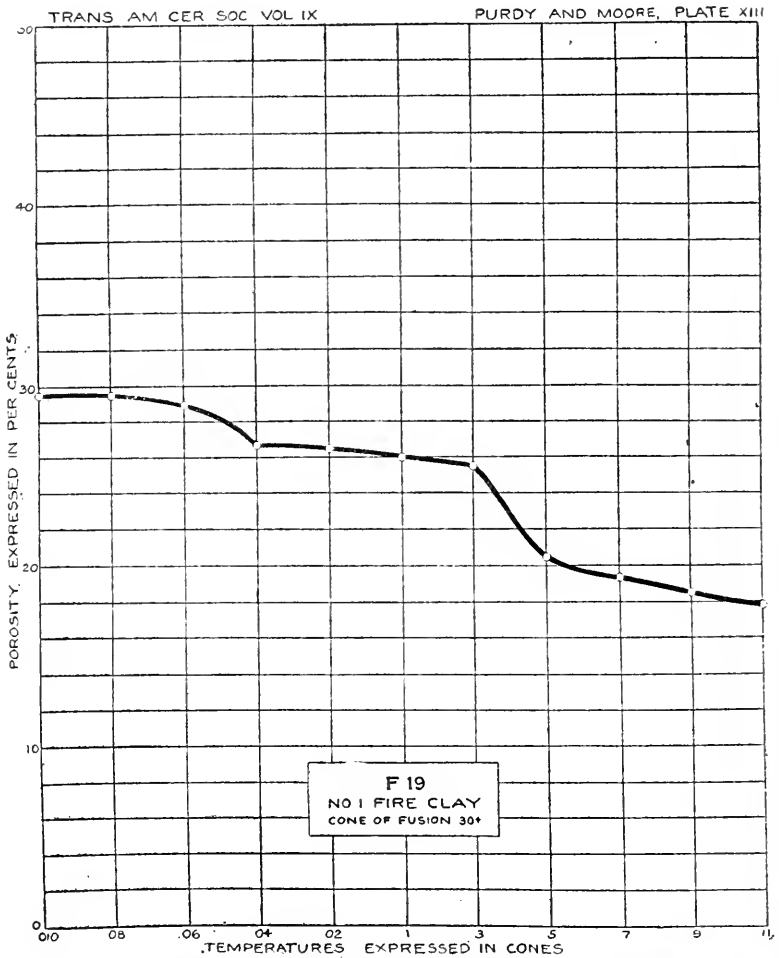
Curve showing changes in porosity of clay V 2, at different temperatures.
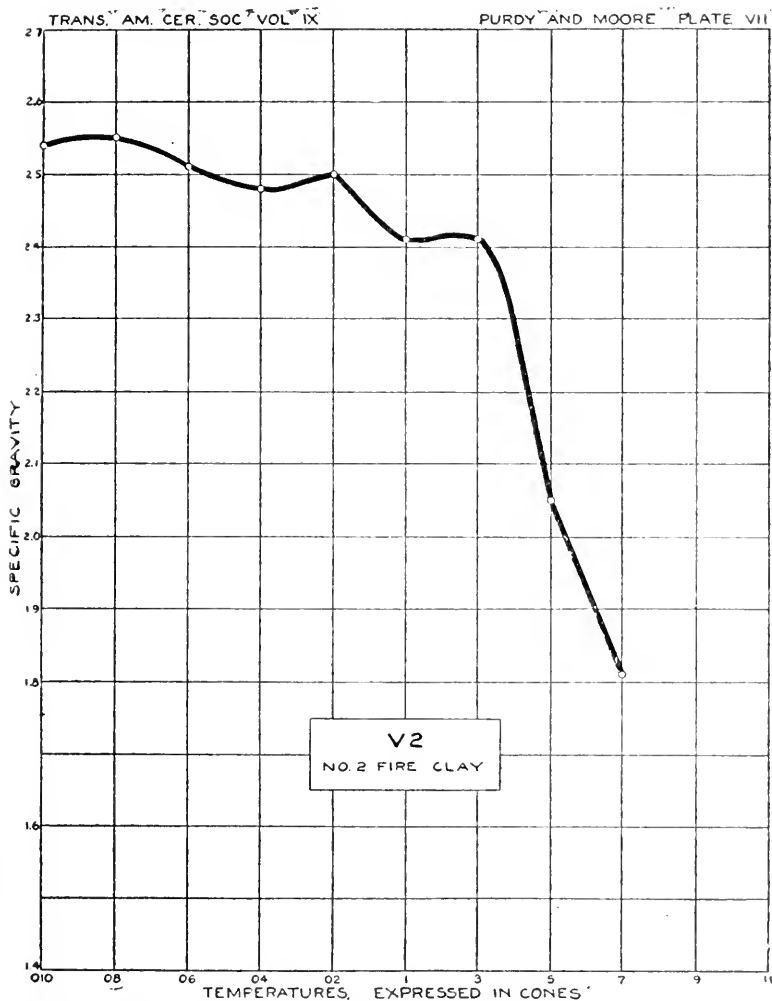
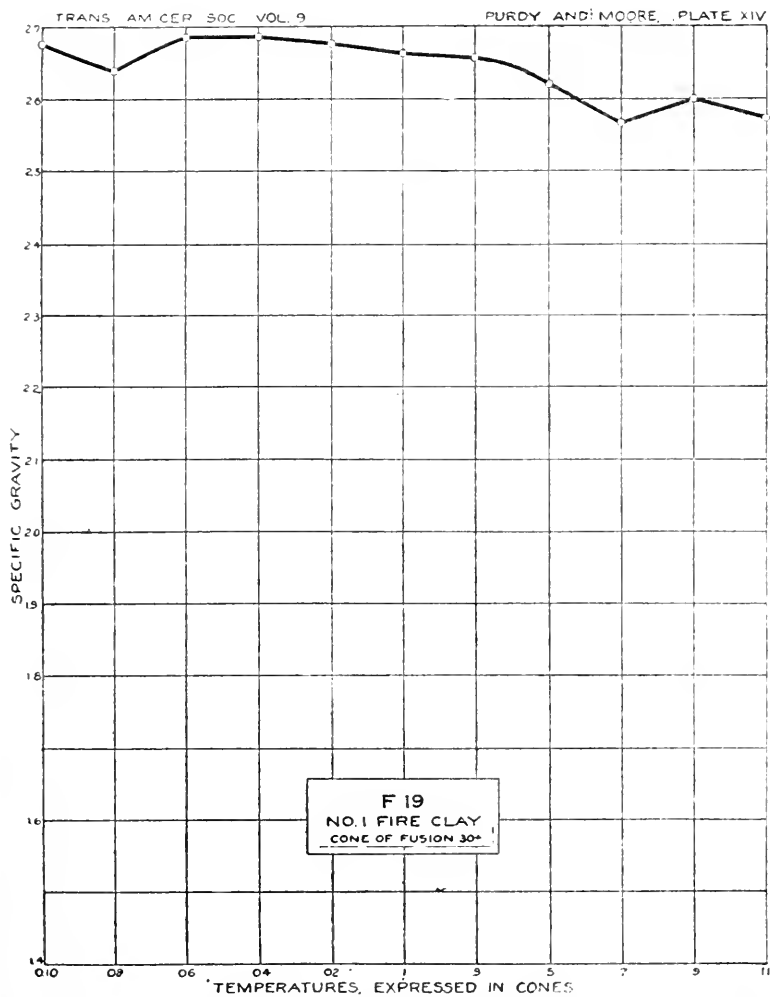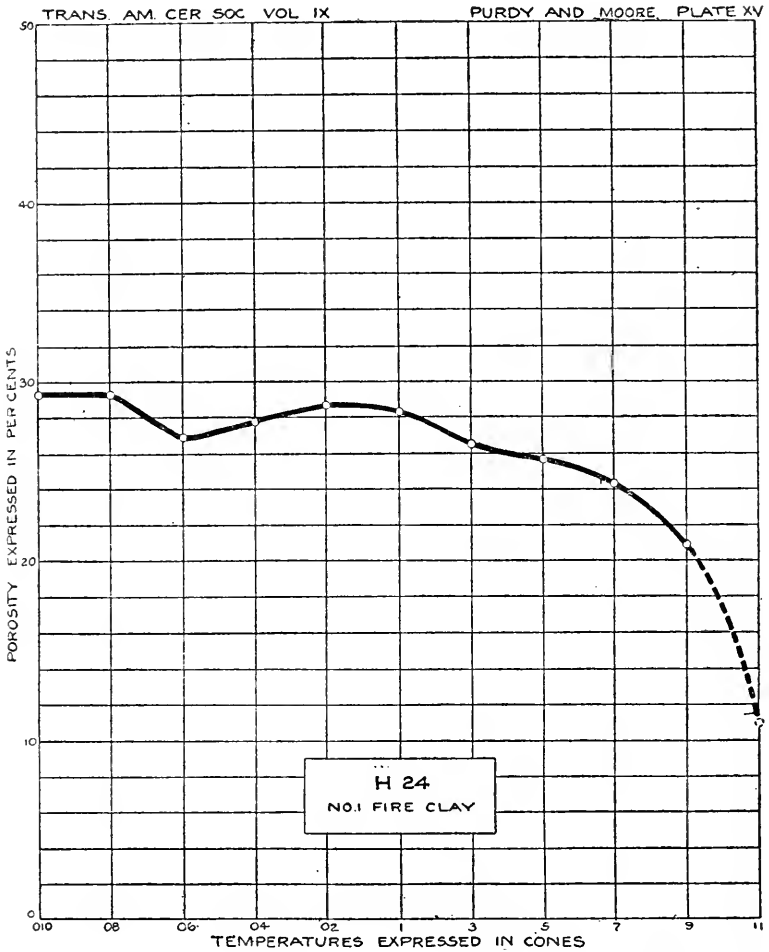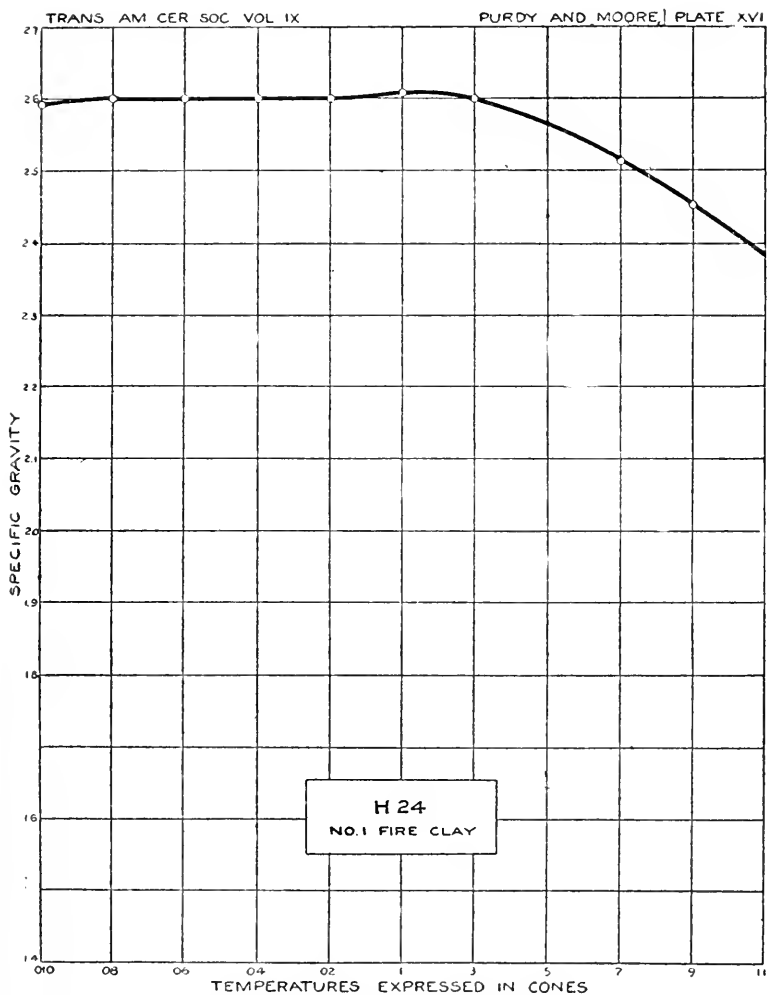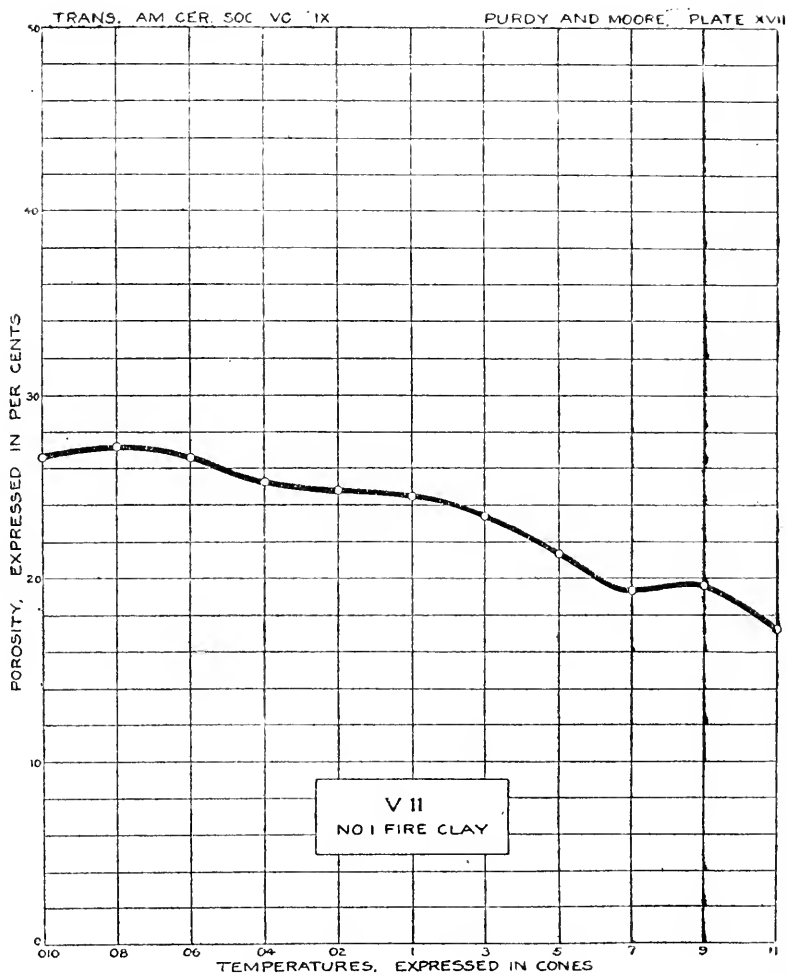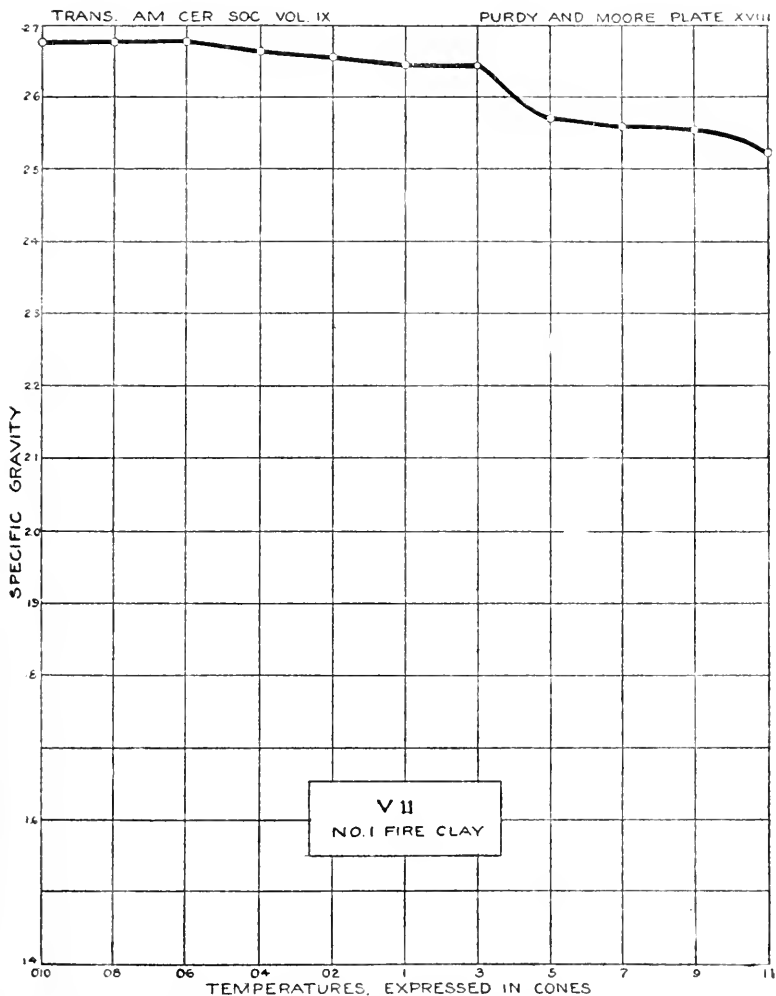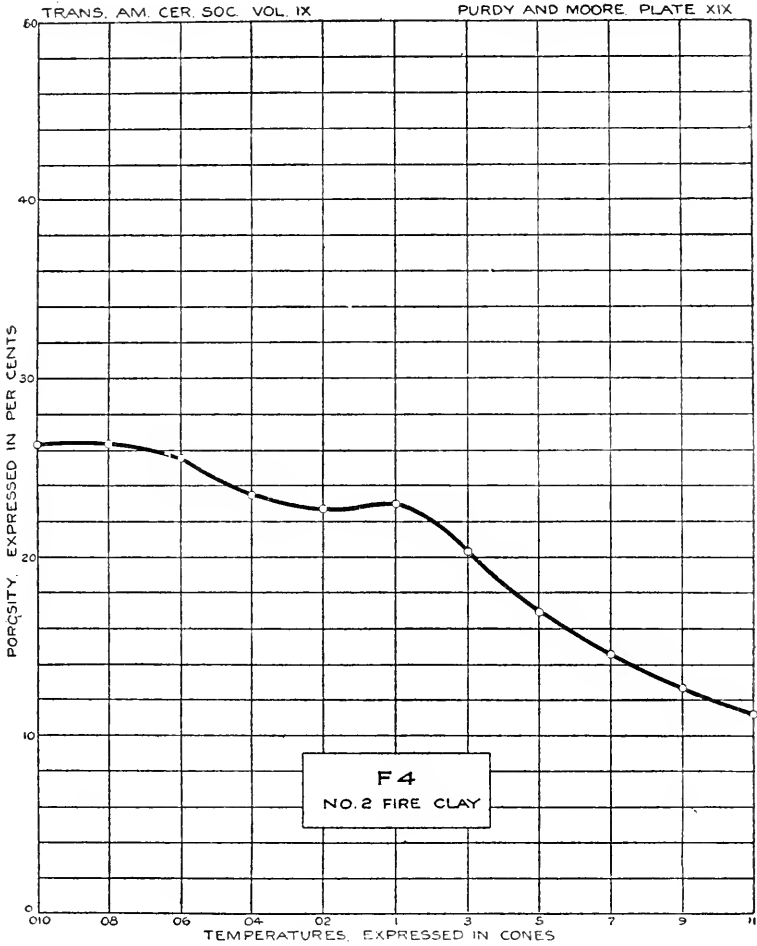Curve showing changes in specific gravity of clay V 2, at different temperatures.

While such clays vitrify too rapidly to produce tough bricks, such as are demanded for street paving, they become impervious to water at low temperatures and do not soften by fusion with increase of heat ranging over several cones, or swell because of the generation of gases from the interior of the brick. In other words, while bricks made from such clays are brittle, they are rendered hard and impervious to water at comparatively low temperatures, and at the same time have a relatively wide heat range before failing by complete fusion, or becoming distorted by expansion of gases in their interior.

The writers have not had sufficient experience with this method of classification to justify them in offering a complete scheme for the grouping of clays, and have therefore suggested only five classes.

NUMBER ONE FIRE CLAYS.

The writers of Clay Reports have heretofore failed to recognize that of two clays having similar ultimate chemical compositions and similar ultimate fusion periods, one can be used in No. 1 fire brick, while the other would fail utterly as a fire brick material, and that the one failing as a fire brick material would be the only one that could with success be used in the stone ware industry. Several examples of the foregoing were noted in the examination of the Illinois fire clays. In fact, the case is not an uncommon one.

In fire brick, maintenance of an open structure through the entire heat range used in the various ceramic industries is essential. On the other hand, in stoneware, closeness of structure at comparatively low temperatures, or early vitrification followed by a long fusion range is absolutely required. It is evident, therefore, that a classification of refractory fire clays (so called because they withstand heat equivalent to cone 27 or more without failure) should take account of this difference in their manner

of fusion. This essential difference in the behavior of fire clays is recognized in the tentative scheme of classification here presented.

It will be noted that these clays show comparatively little decrease in porosity from cone 010 to cone 11. This decrease averages from 7 to 15% of the initial porosity and in no case does it exceed 17%.

The specific gravity remains fairly constant from cone 010 to cone 3, and then, even in the purest clays, it begins to decrease slightly. This decrease in specific gravity in the No. 1 fire clays, even when the porosity remains very high, is considered as evidence of the influence of the adsorbed or cementing salts which, while constituting but a very small part by weight of the whole, are nevertheless the potent factor in causing fusion.

The chemical composition and ultimate fusion point of these clays as determined in the chemical laboratory of the University of Illinois, under the supervision of Professor S. W. Parr, are as follows:

Sample Number	Moisture	Volatile Matter	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Total	Fusion point
H. 24	0.6	4.63	76.10	15.31	1.10	1.31	99.06	30
V. 11	1.74	10.28	56.28	26.68	3.24	1.29	99.50	Not reached
F. 18	0.84	6.66	66.88	21.87	2.23	1.18	99.86	29
F. 19	1.19	6.31	68.12	20.08	1.76	1.16	98.62	31
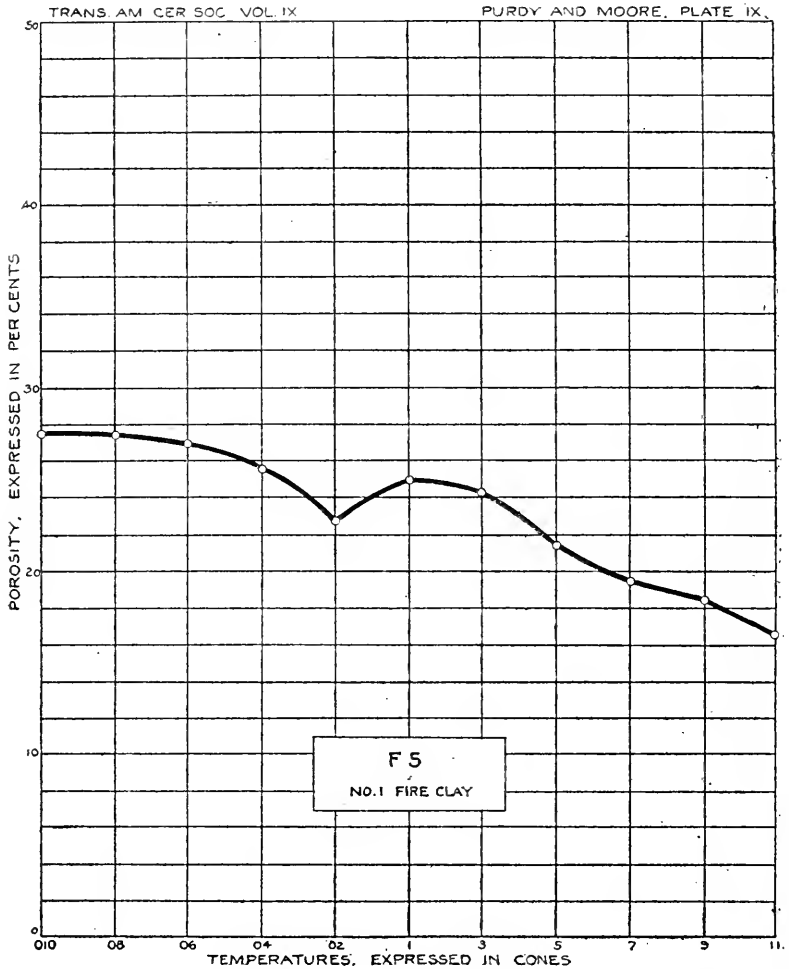
Curve showing changes in porosity of clay F 5, at different
temperatures.
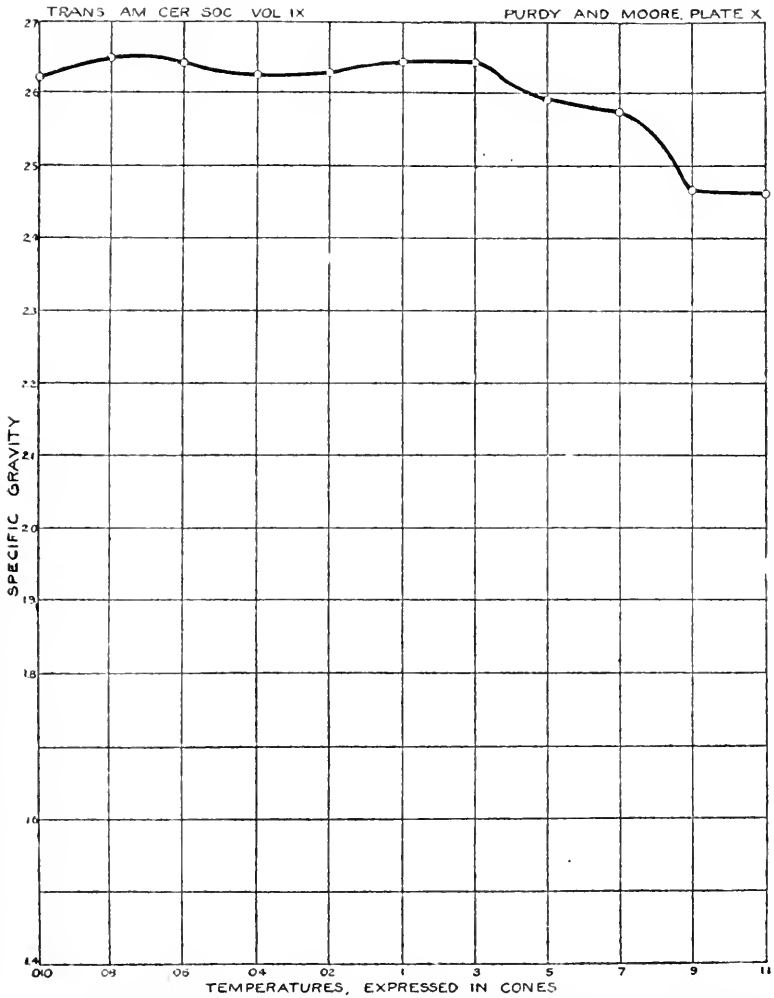
Curve showing changes in specific gravity of clay F 5 at different temperatures.
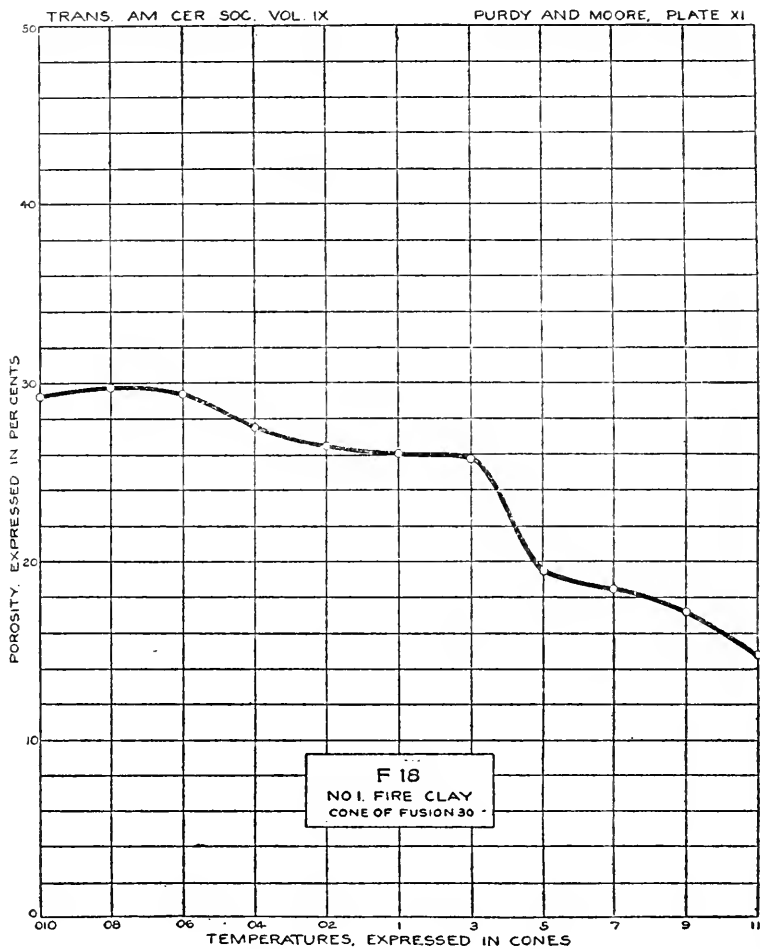
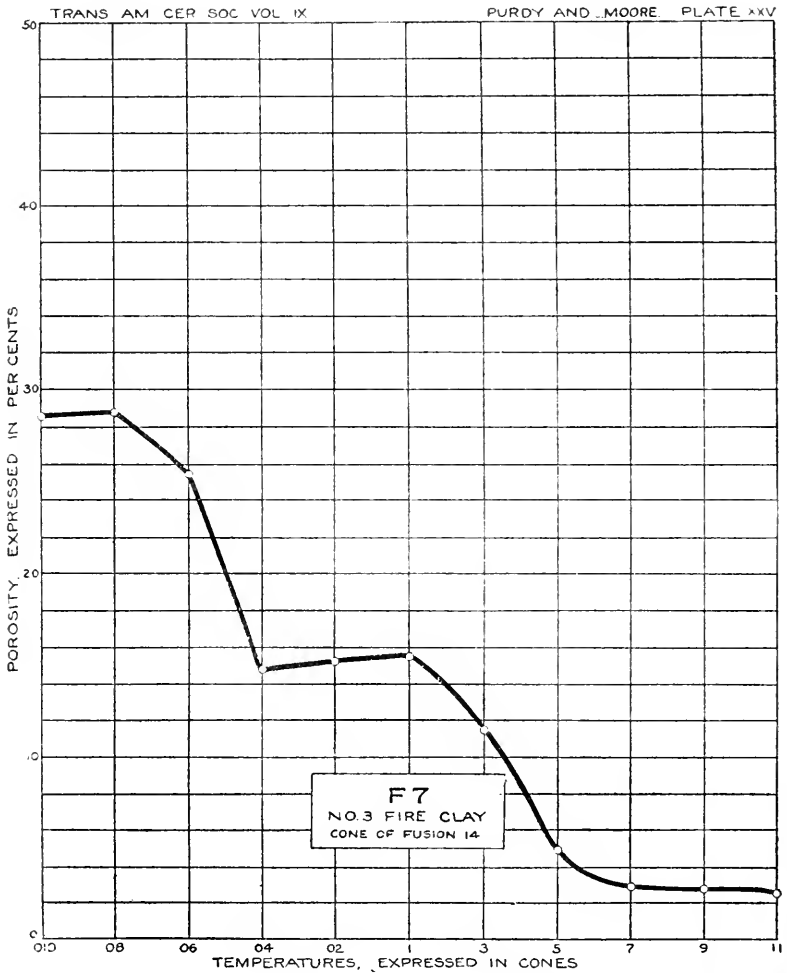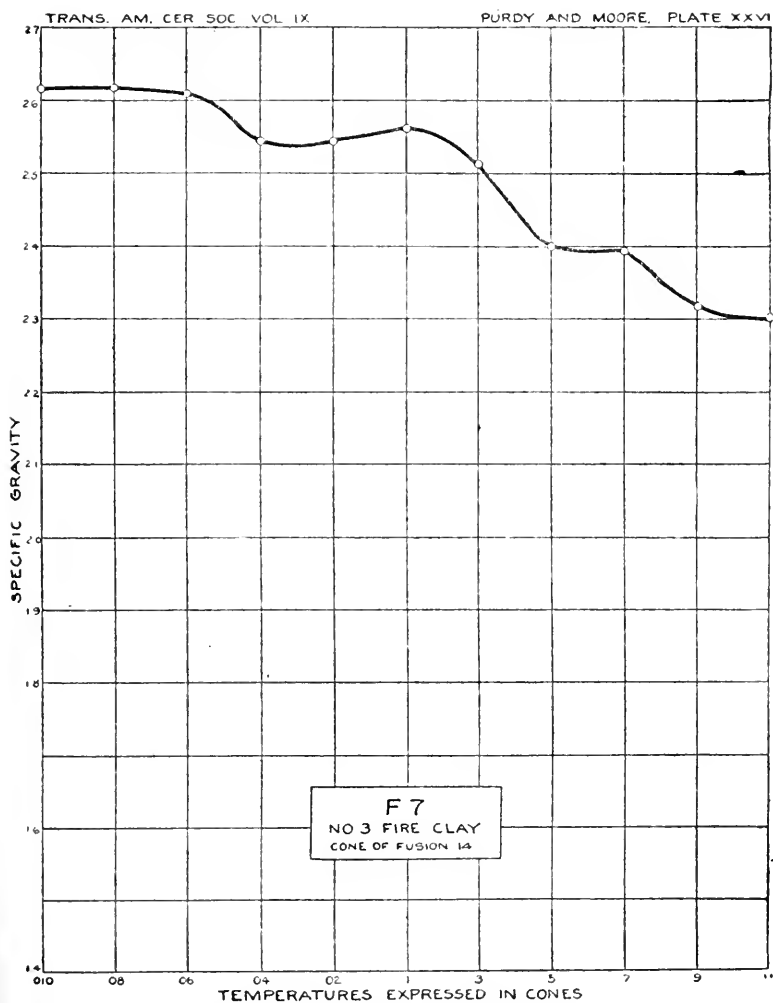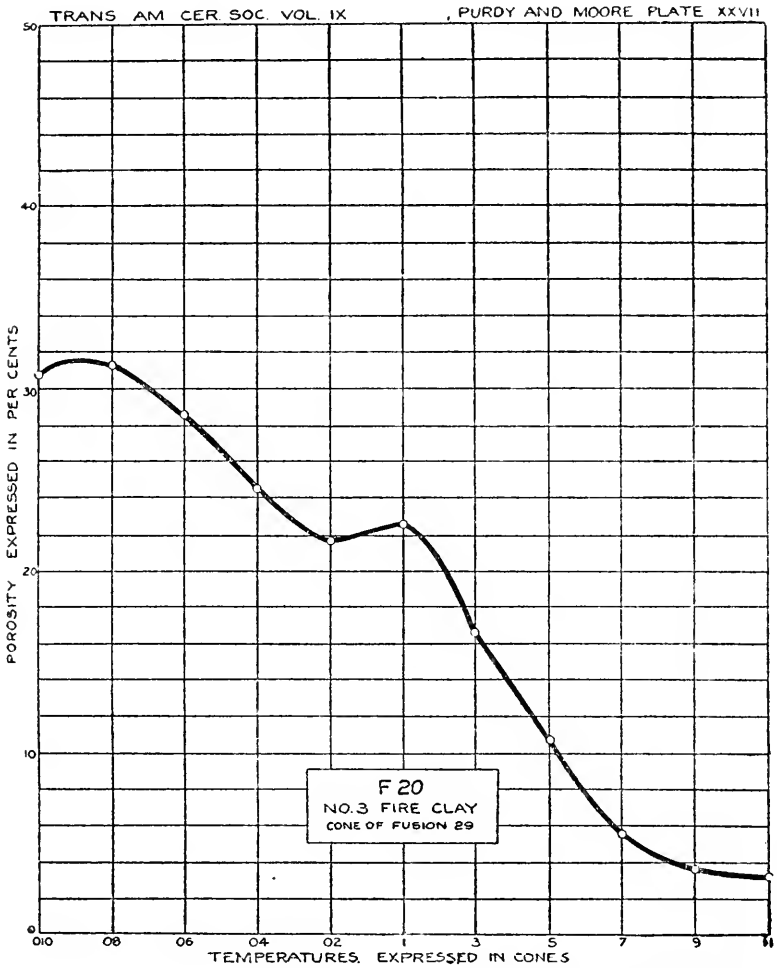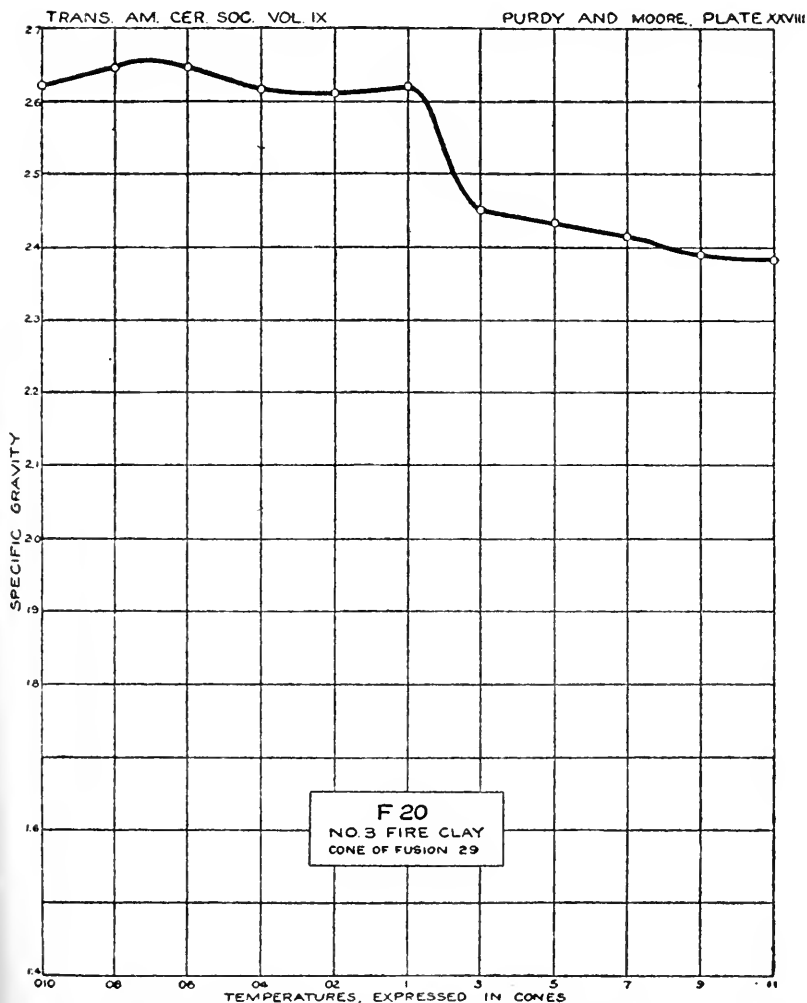Curve showing changes in porosity of clay F 18, at different
temperatures.

TRANS AM CER SOC   VOL IX   PURDY AND MOORE, PLATE XII

F 18
NO. I FIRE CLAY
CONE OF FUSION 30.

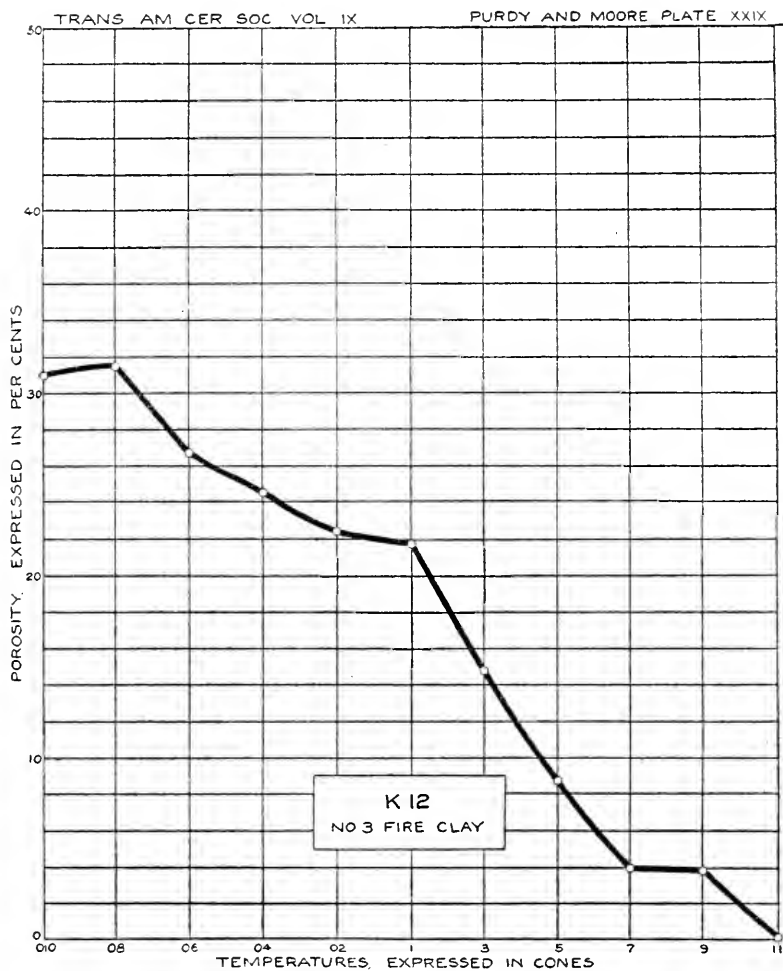SPECIFIC GRAVITY

TEMPERATURES, EXPRESSED IN CONES

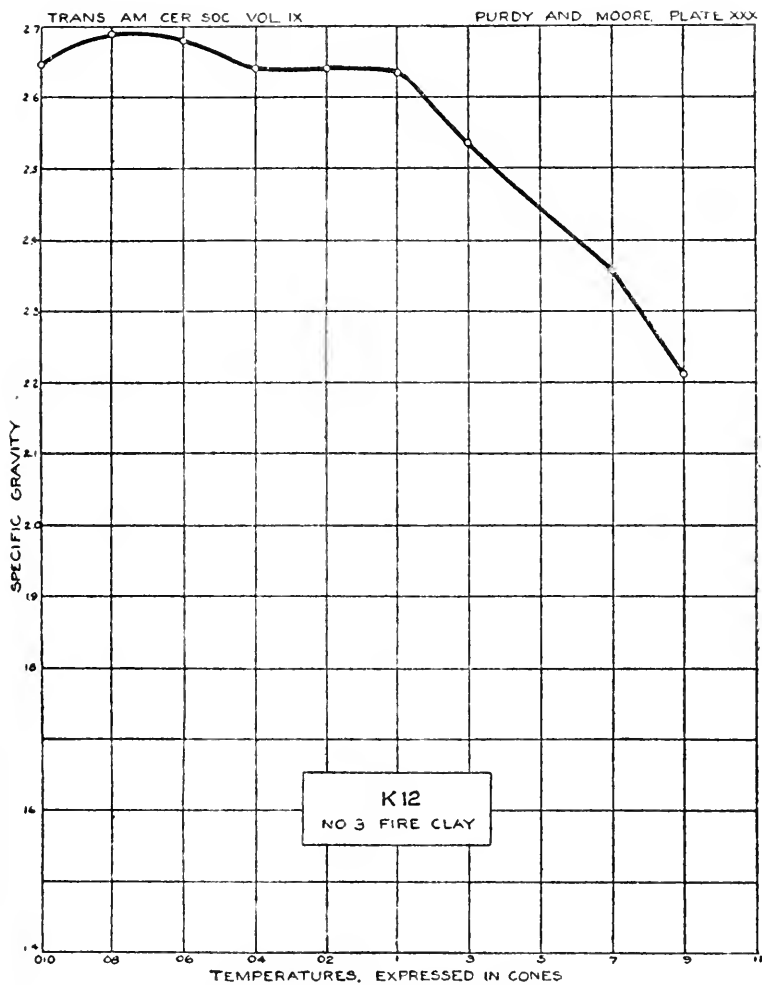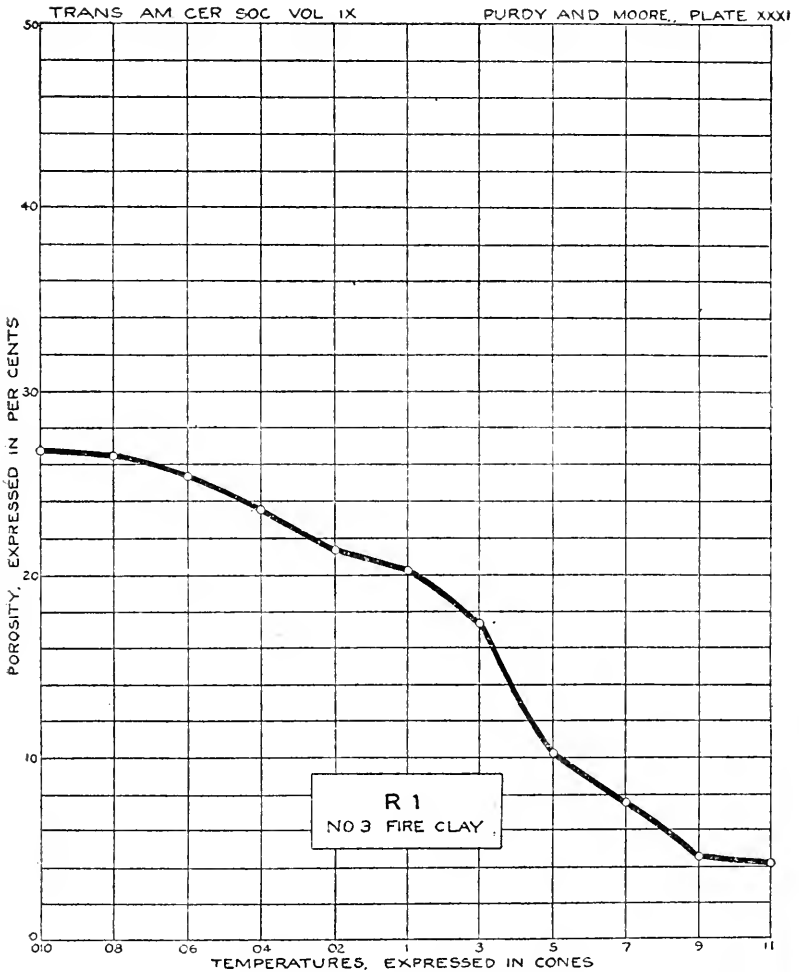Curve showing changes in specific gravity of clay F 18, at different
temperatures.
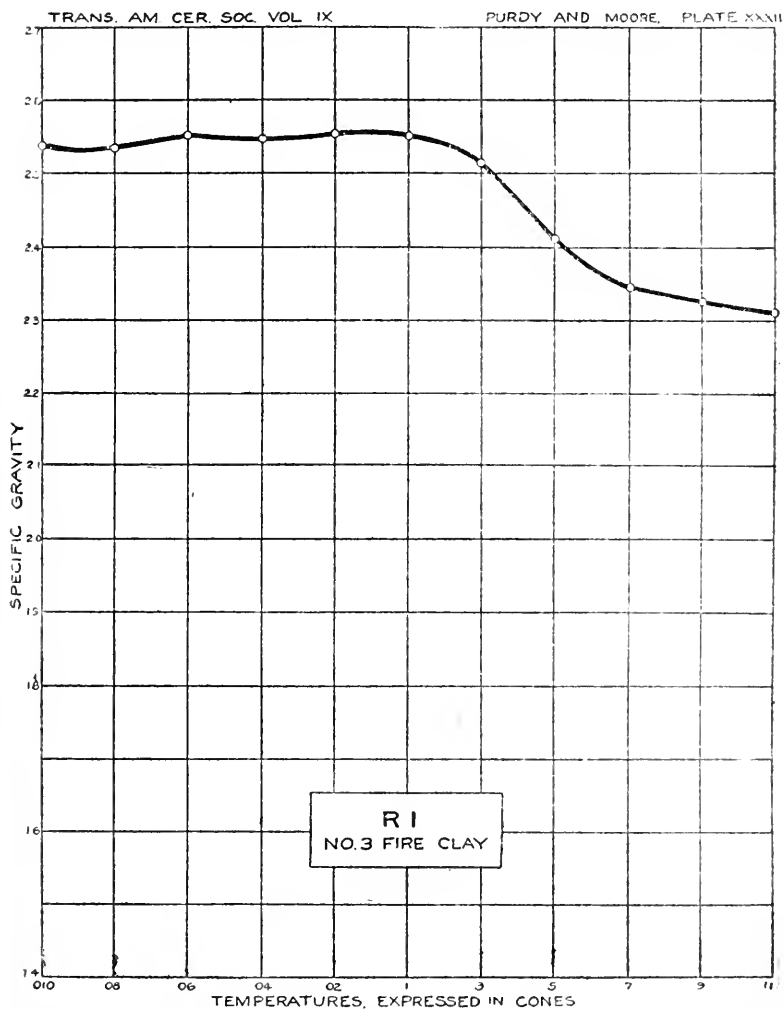
Curve showing changes in porosity of clay F 19, at different
temperatures.

Curve showing changes in specific gravity of clay F 19, at different temperatures.

Curve showing changes in porosity of clay H 24, at different temperatures.
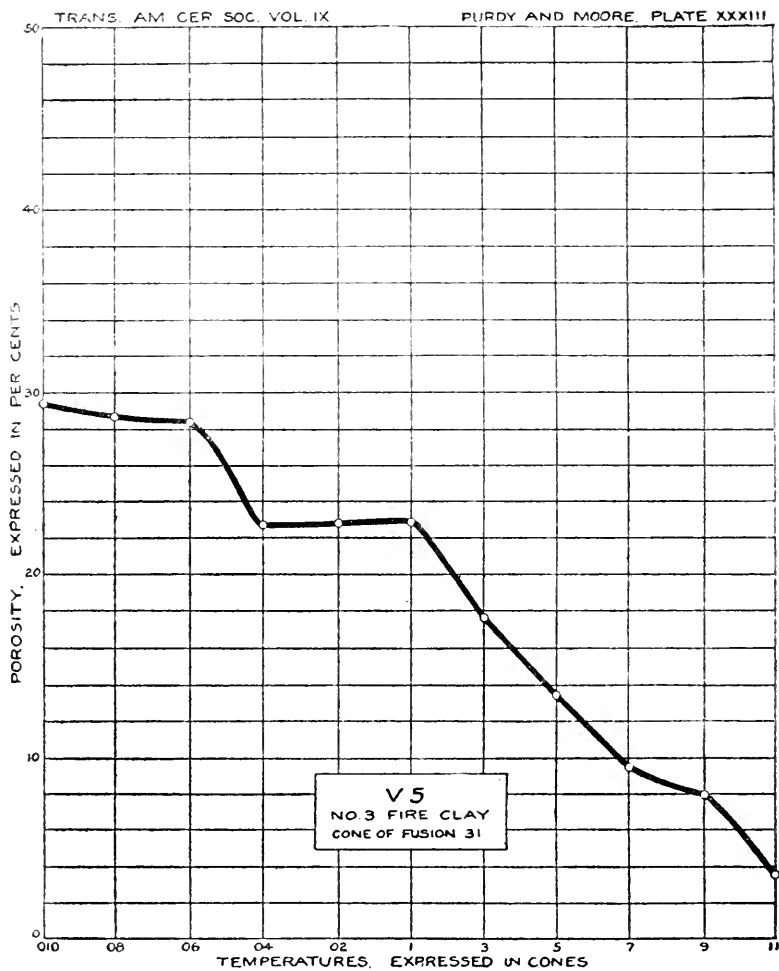
Curve showing changes in specific gravity of clay H 24, at various temperatures.

Curve showing changes in porosity of clay V 11, at various
temperatures.

Curve showing changes in specific gravity of clay V 11, at various temperatures.

NUMBER TWO FIRE CLAYS.

A few number two fire clays are represented in the following collection of plates. It will be noted that while the decrease in specific gravity of this group of clays is about the same as that shown in the No. 1 fire clays, the porosity shows a much larger decrease. The early vitrification and slow fusion is quite pronounced in this group, permitting their use in the paving brick, sewer pipe, stoneware and terra cotta industries, but not in the manufacture of No. 1 fire brick.

The chemical analyses of two of these clays, made in the chemical laboratory of the University of Illinois, under the supervision of Professor S. W. Parr, are as follows:

| Sample Number	Moisture	Volatile Matter	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Total	Fusion point
V. 4	2.37	8.84	54.80	29.44	1.70	0.82 fluxes	97.97	not reached
K. 12	0.60	10.09	54.37	23.61	6.14	5.97	100.78	not deter'ed

Curve showing changes in porosity of clay F 4, at different temperatures.
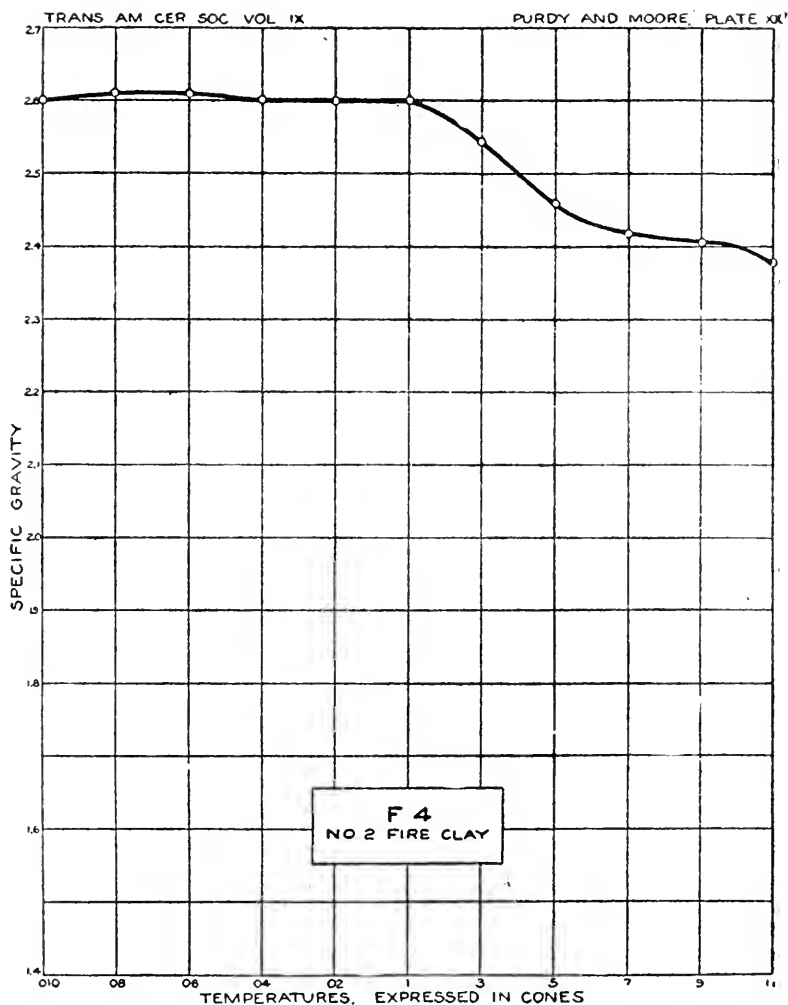
Curve showing changes in specific gravity of clay F 4, at different temperatures.
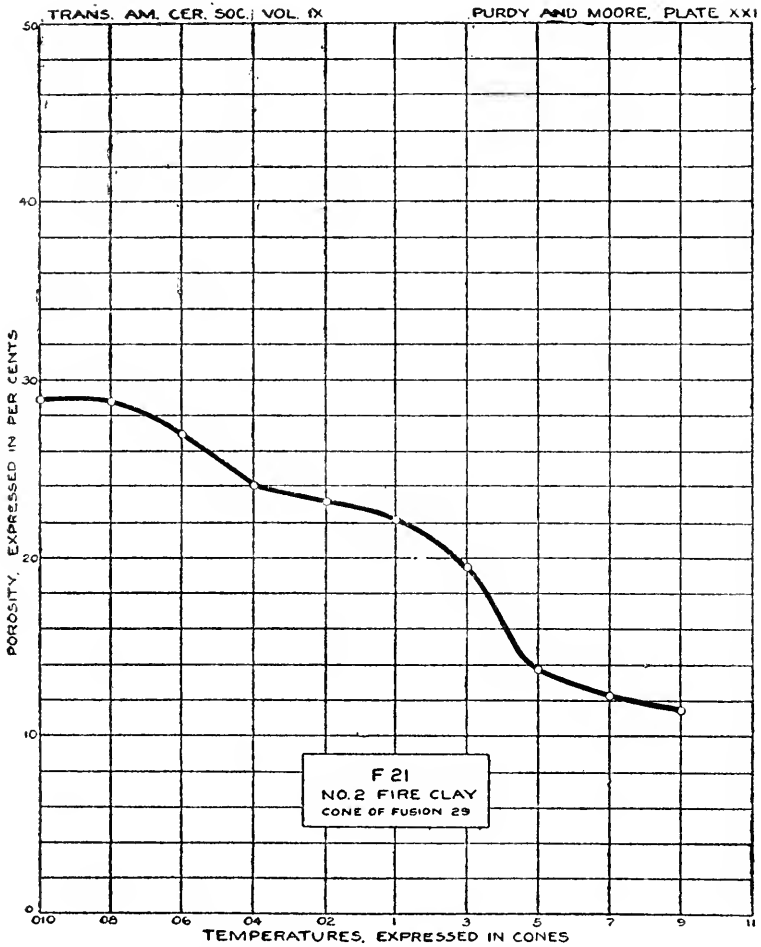
Curve showing changes in porosity of clay F 21, at different
temperatures.
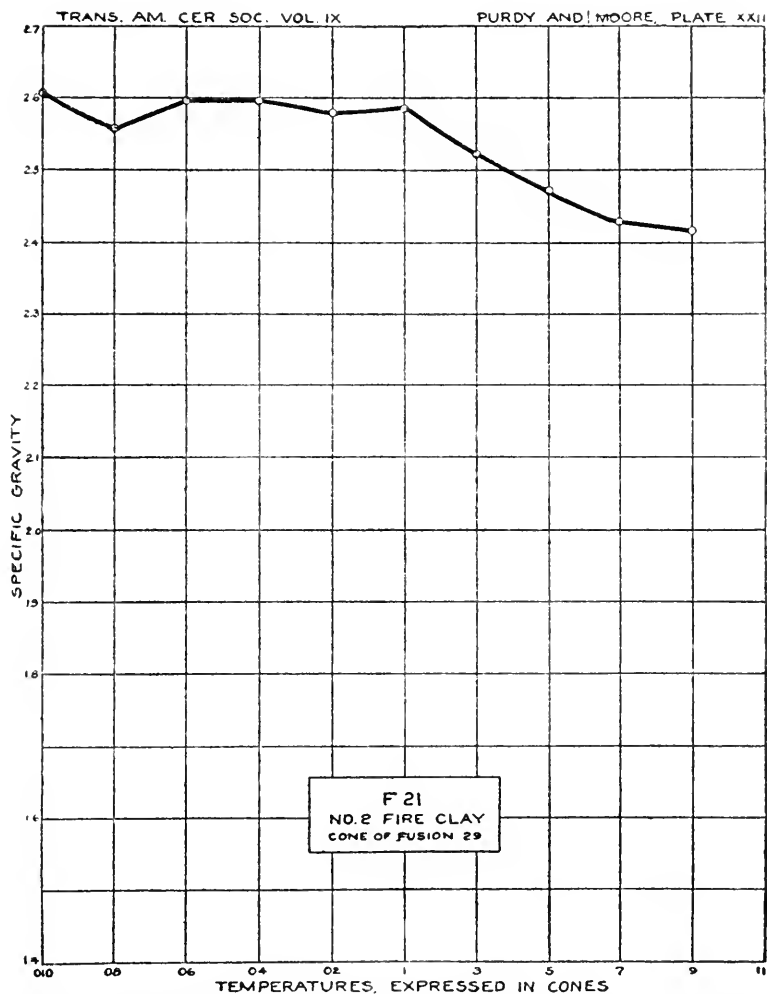
Curve showing changes in specific gravity of clay F 21, at different
temperatures.
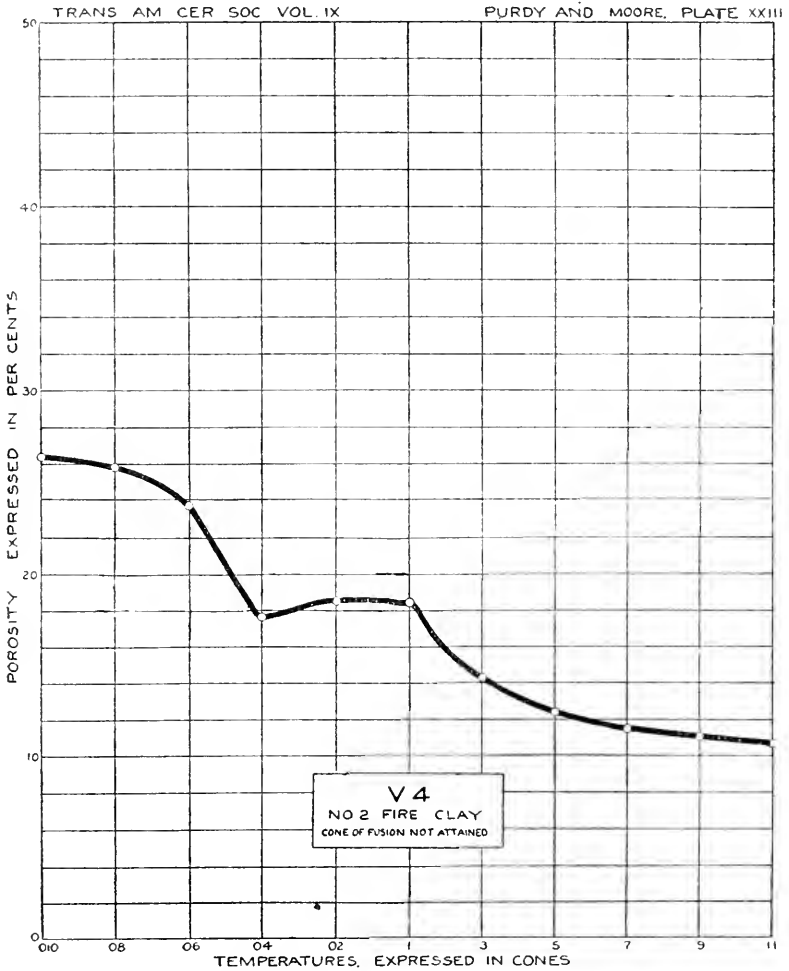
Curve showing changes in porosity of clay V 4, at different
temperatures.
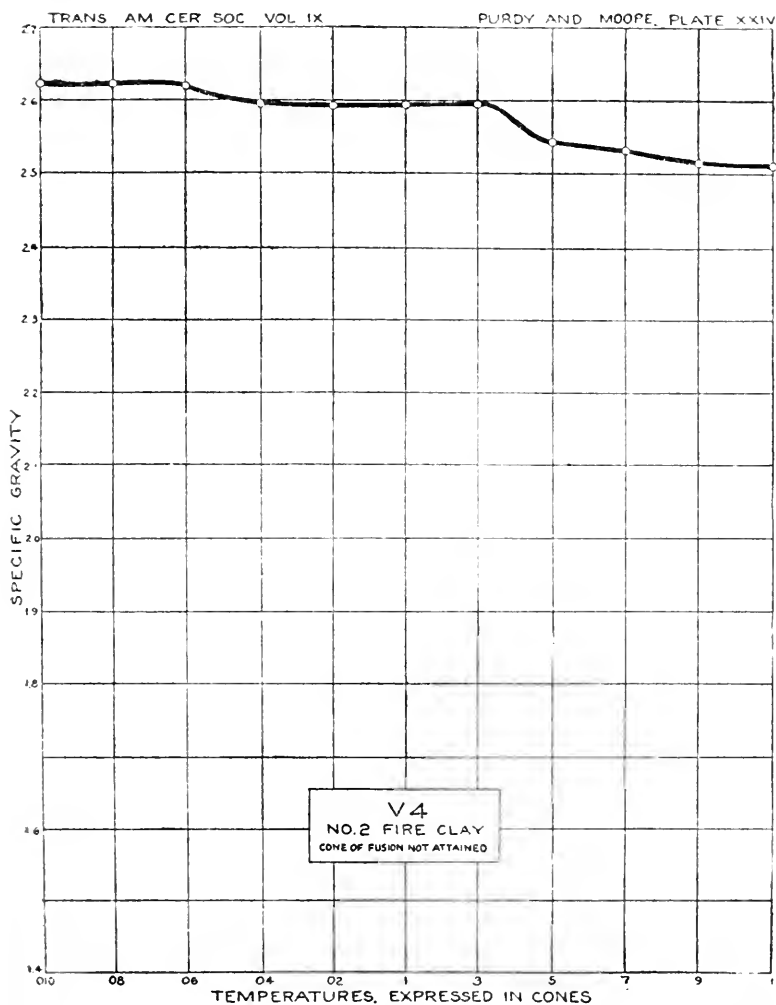
Curve showing changes in specific gravity of clay V 4, at different
temperatures.

NUMBER THREE FIRE CLAYS.

In the following ten pages are shown the porosity and specific gravity curves of a class of clays which in the judgment of the writers, ought to be put in a different catagory from the preceding group or number two fire clays. Heretofore, both have been classified together indiscriminately in ceramic and geological literature, as number two fire clays, but they are not the same. Clays of this class differ from the No. 1 and No. 2 fire clays, in that they seldom have a fusion point exceeding cone 16 or 17, fuse in a very irregular manner, and exhibit a much larger decrease in specific gravity owing to the presence of iron in nodular form as sulphides or carbonates.

F 7
NO.3 FIRE CLAY
CONE OF FUSION 14

Curve showing changes in porosity of clay F 7, at different
temperatures.

Curve showing changes in specific gravity of clay F 7, at different
temperatures.

Curve showing changes in porosity of clay F 20, at different temperatures.

Curve showing changes in specific gravity of clay F 20, at different
temperatures.

Curve showing changes in porosity of clay K 12, at different temperatures.

Curve showing changes in specific gravity of clay K 12, at different temperatures.

Curve showing changes in porosity of clay R 1, at different temperatures.

Curve showing changes in specific gravity of clay R 1, at different
temperatures.

Curve showing changes in porosity in clay V 5, at different
temperatures.
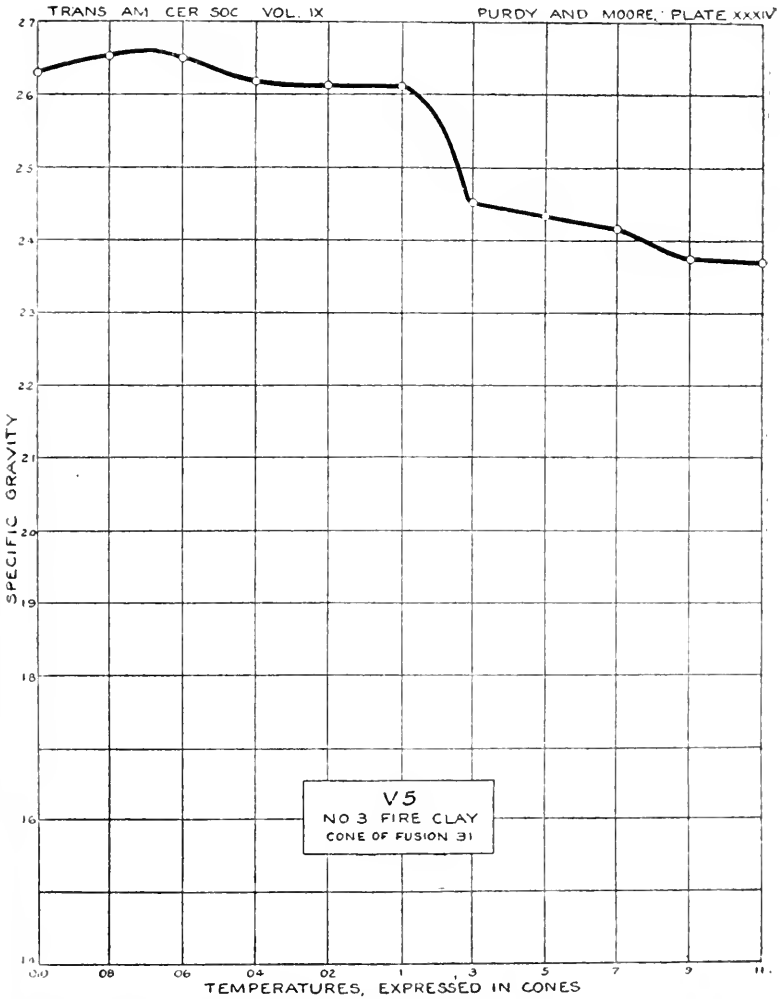
Curve showing changes in specific gravity of clay V 5, at different temperatures.

SUMMARY OF FIRECLAY GROUP.

The manner and amount of decrease in porosity and specific gravity between these three groups is quite marked. Similar curves drawn from data obtained on clays other than those here reported, exhibited similar differences.   In the laboratory the clays were known only by sample number, the field data being ignored to prevent possible prejudice, but in no case did the inferred "possible uses" of the clay disagree with data obtained in the field concerning their commercial use at the present time.   So far then, as the evidence thus obtained is concerned, it can be stated that this method of classifying fire clays has succeeded where other methods have failed.

PAVING BRICK SHALES.

The standardization of tests for first class paving brick clays has been and perhaps will be for some time ing brick clays has been and perhaps will be for some time the subject of much consideration by ceramic investigators. The tests here reported can be said to give negative rather than positive information, in that they very effectively differentiate the clays that *cannot* from those which *may* be utilized in paving brick manufacture. Judging from the results so far obtained, they fail, however, to differentiate the paving brick clays one from another in regard to their comparative quality. For example, we have not been able to distinguish by these tests between the clays of 14% type and the 24% type, measured in percents of loss in the rattler test, nor between the clays that preserve their maximum strength through a wide heat range and those which attain and preserve their maximum strength only within a very narrow heat range.

The cause of failure of the pyro-chemical studies in this respect is, no doubt, to be found in the fact that inherent strength is not wholly a function of rate of vitrification or development of vesicular structure. Tensile strength of the raw clay, fineness of grain, and many other physical and chemical tests have been made on paving brick clays in order to determine the relation between their properties and the strength of the burned ware, but after a study of 25 paving brick clays from different states, it has been found that but very little relation exists. The pyro-chemical studies here reported are the only ones that give any clue to the toughness or strength of the burned ware.

Pyro-chemical studies similar to those here outlined, together with a determination of the maximum strength and the range temperature in which this maximum strength is developed, would enable the observer to properly classify and differentiate paving brick clays. This, however, amounts to a sub-classification of the paving clays on a basis different from that of the main sub-division.
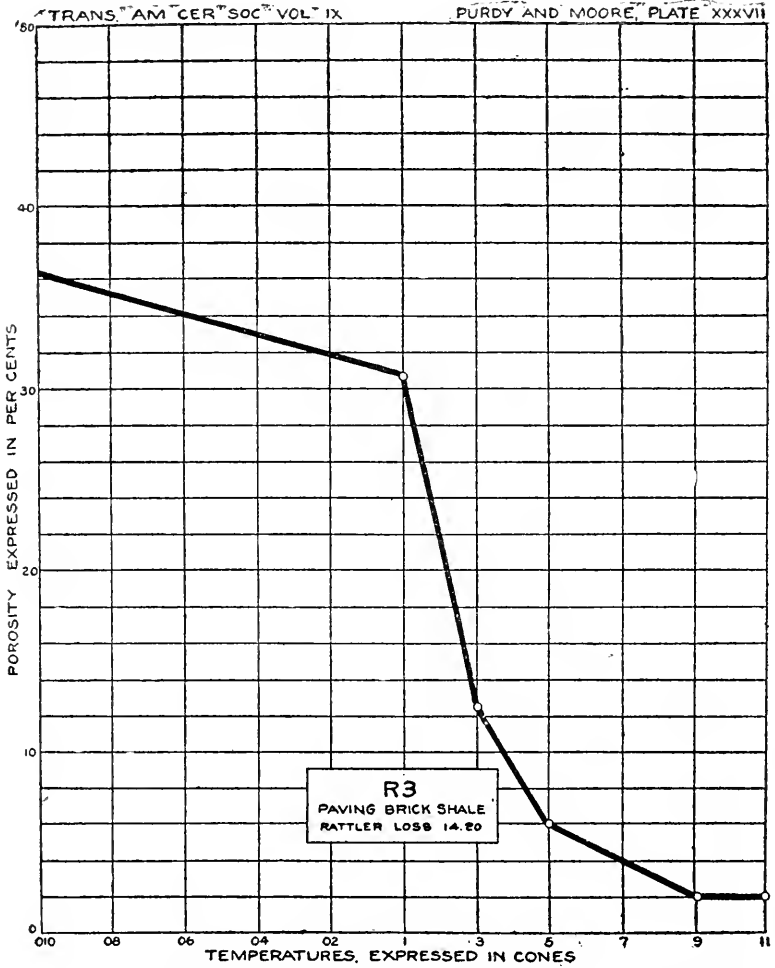
The following are typical porosity and specific gravity curves for clays of the paving brick type:
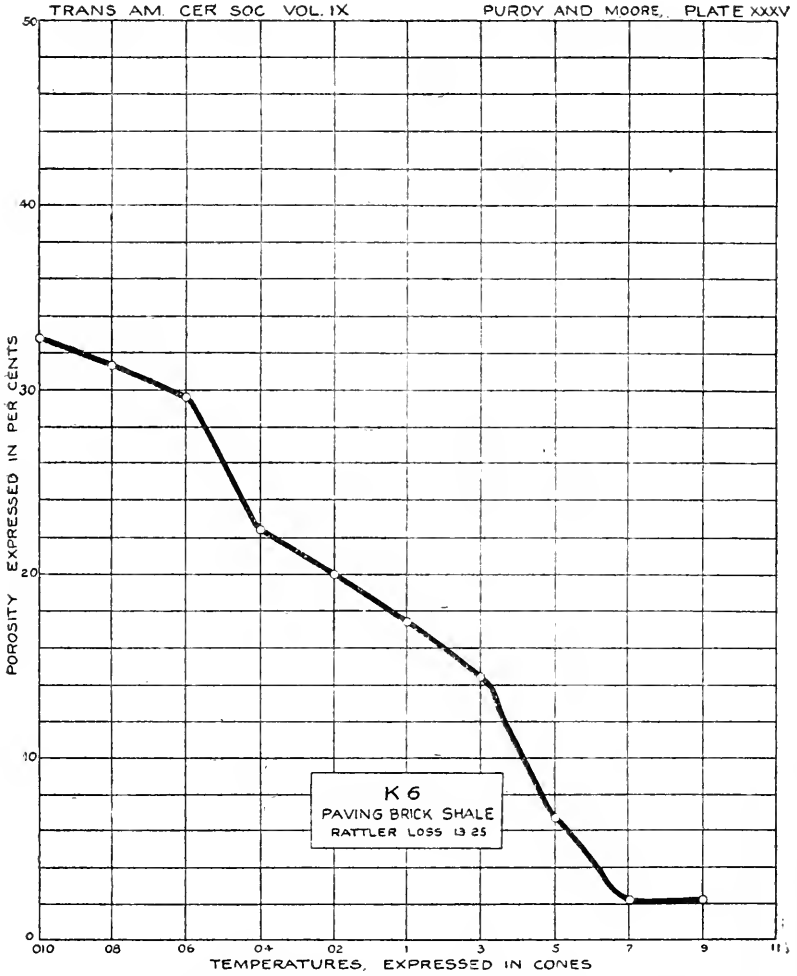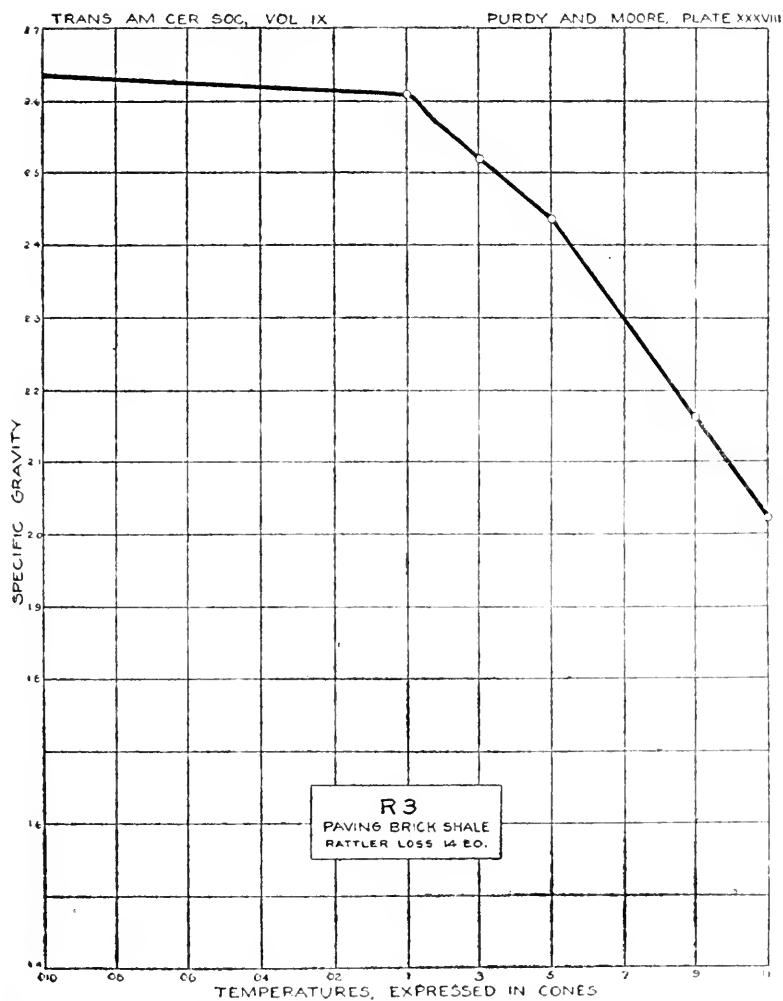
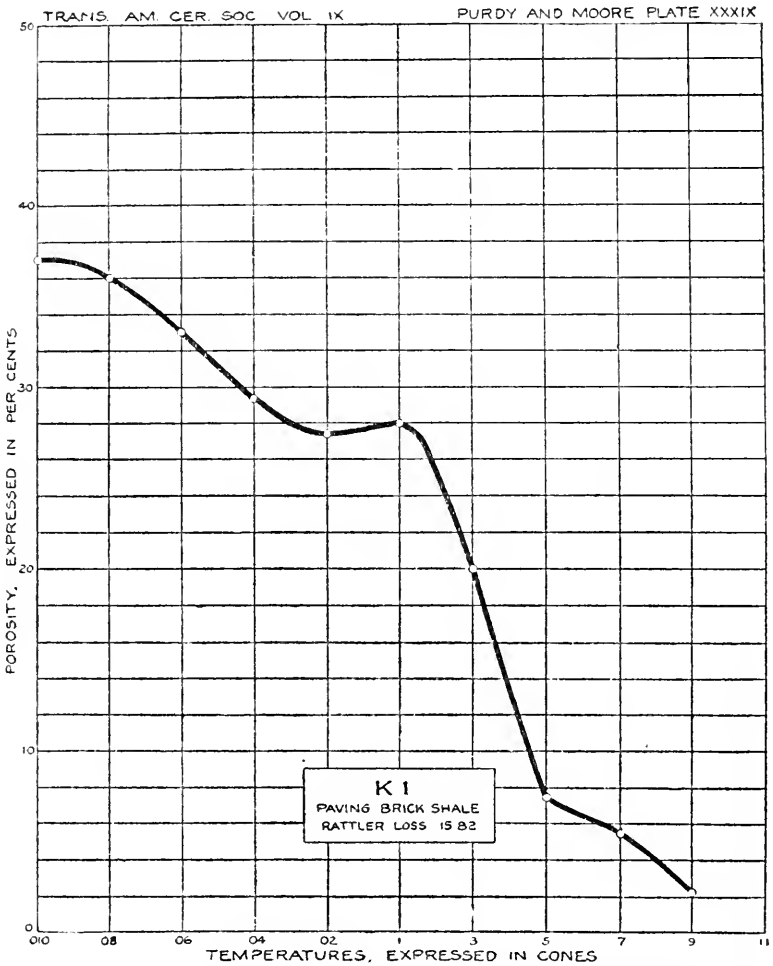Curve showing changes in porosity of clay K 6, at different temperatures.
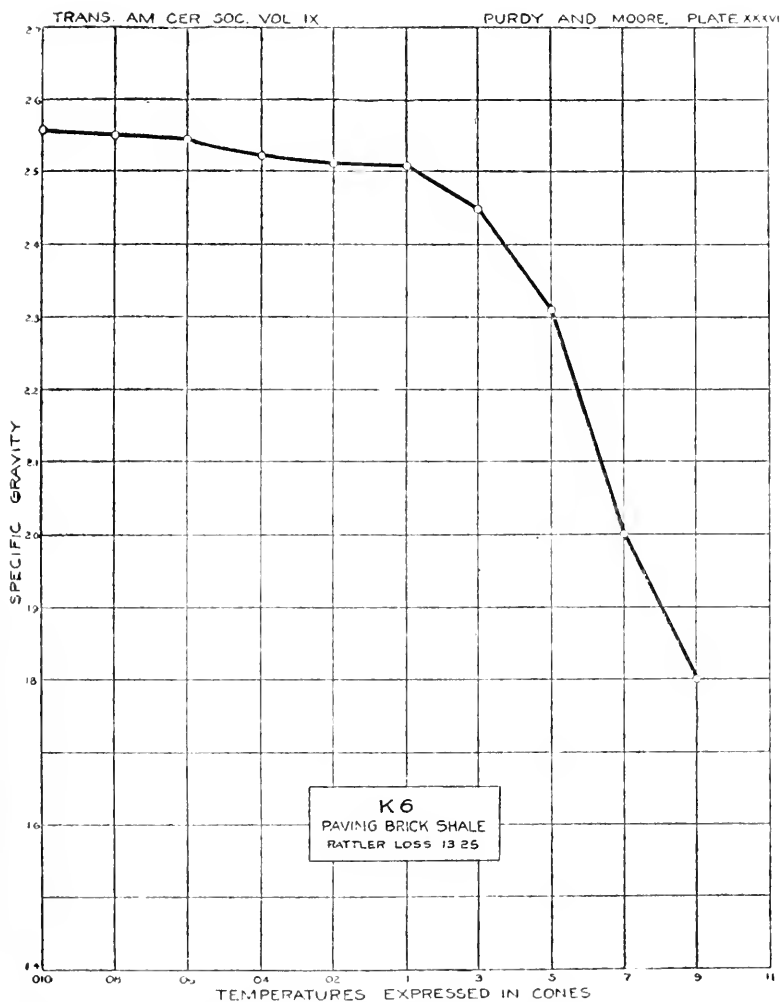
Curve showing changes in specific gravity of clay K 6, at different
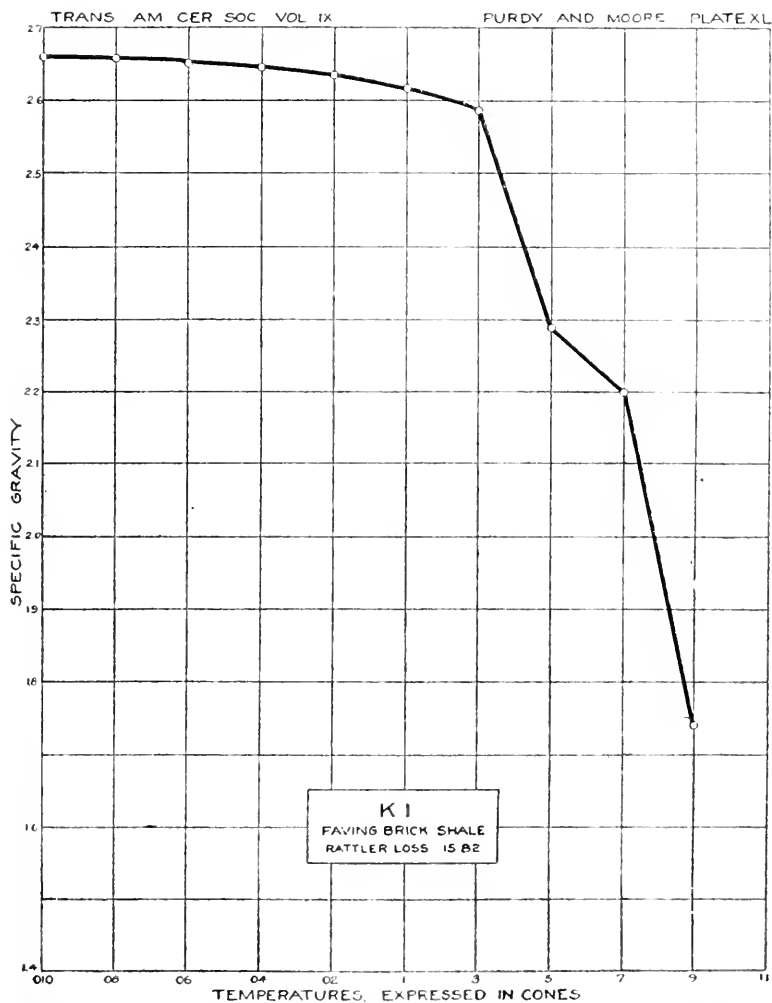temperatures.

Curve showing changes in porosity of clay R 3, at different
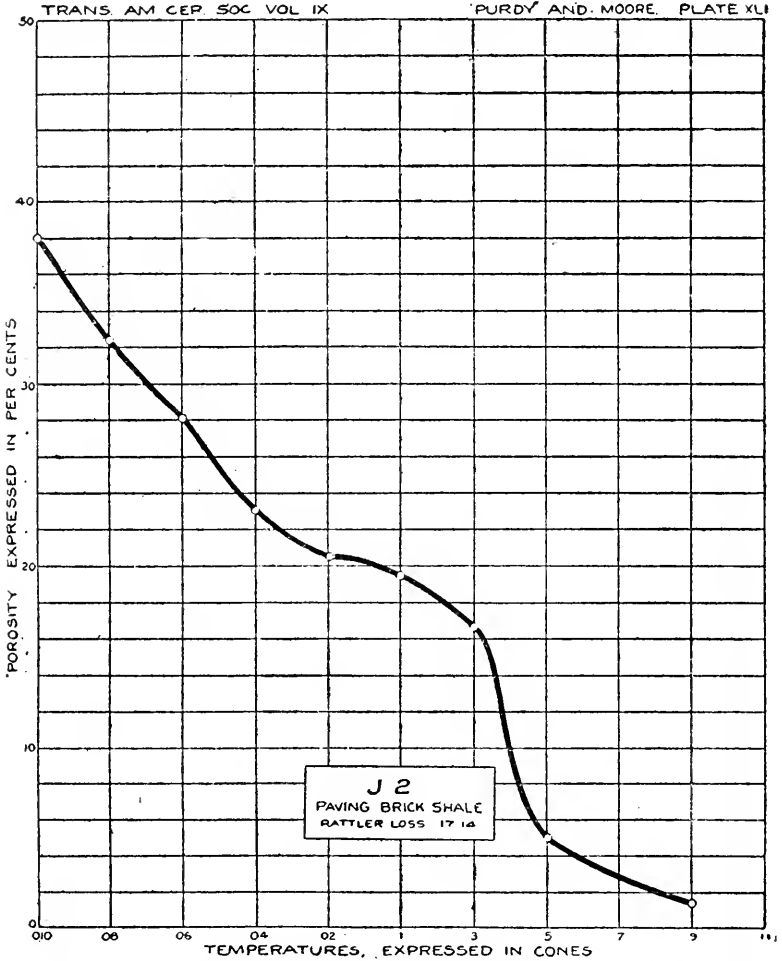temperatures.

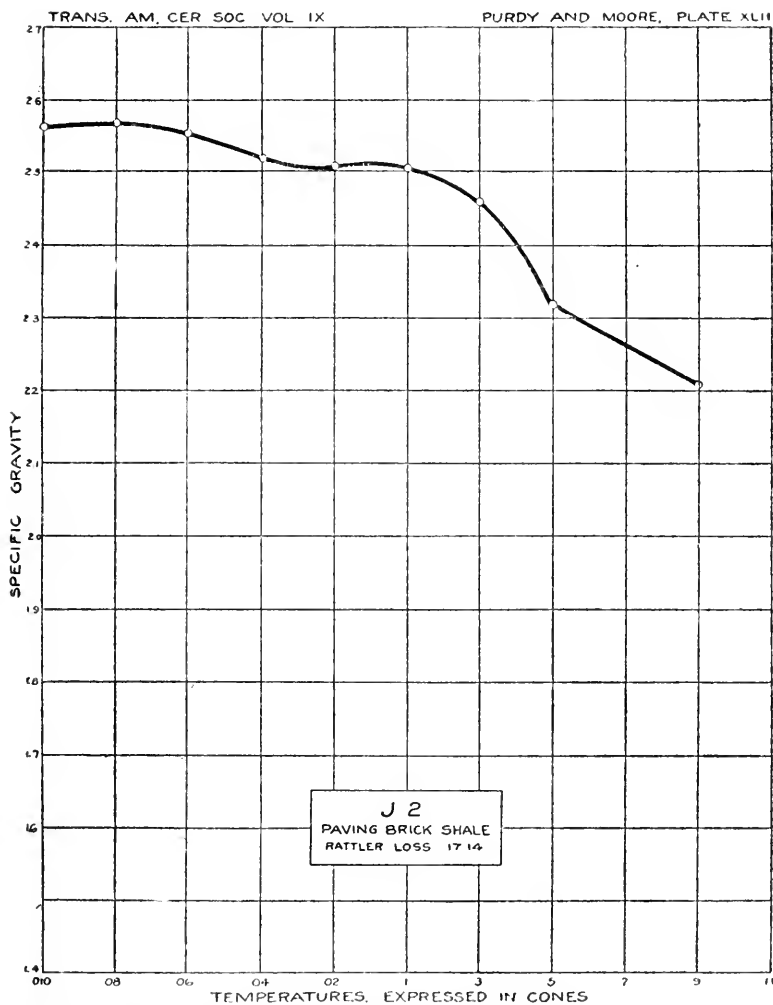Curve showing changes in specific gravity of clay R 3, at different temperatures.

Curve showing changes in porosity of clay K 1, at different
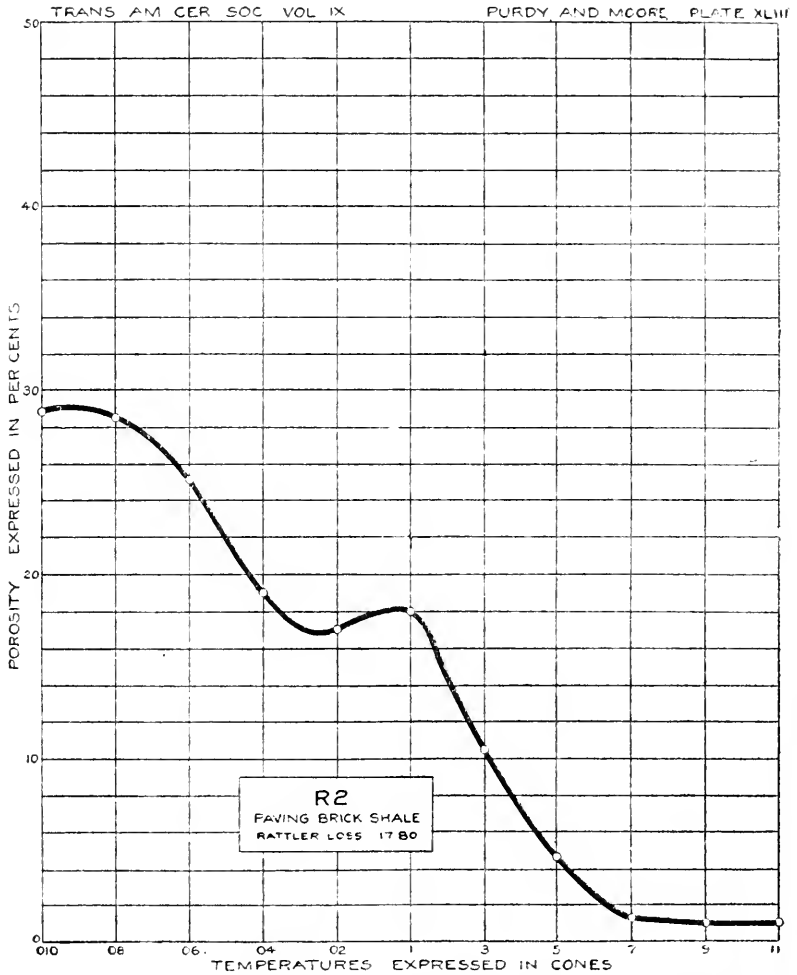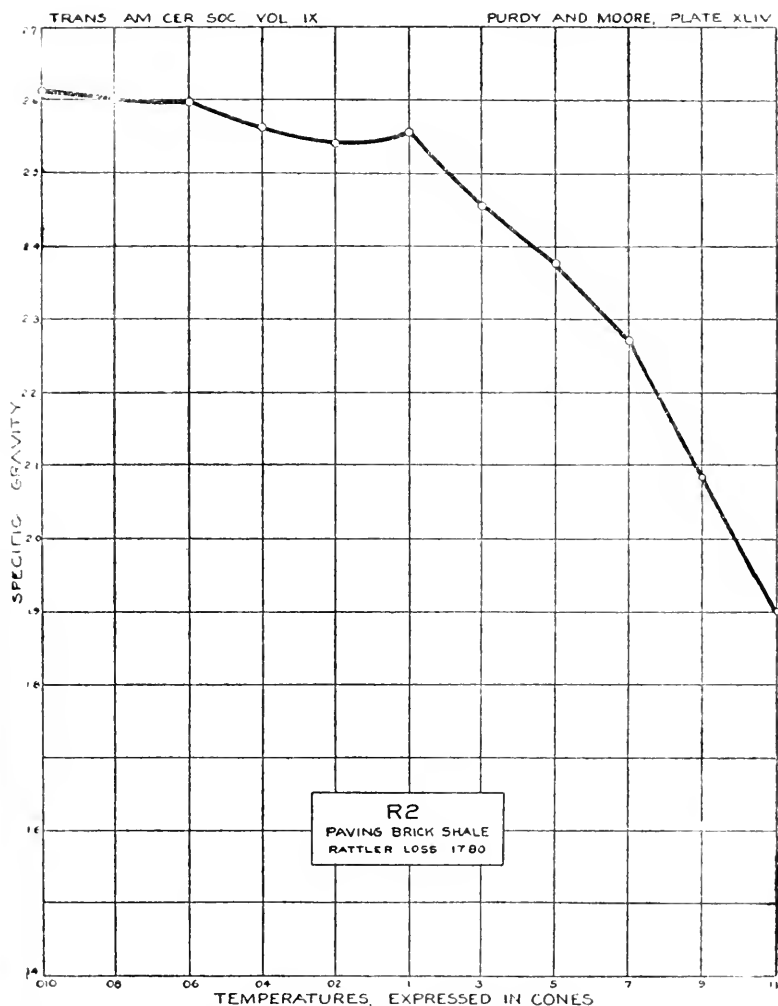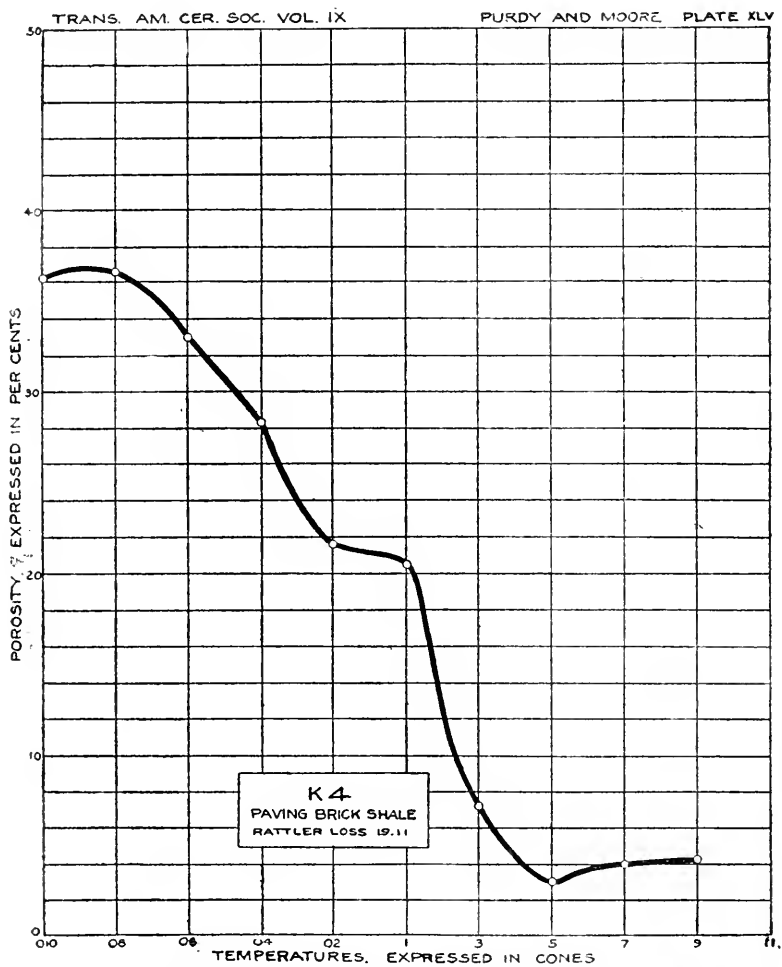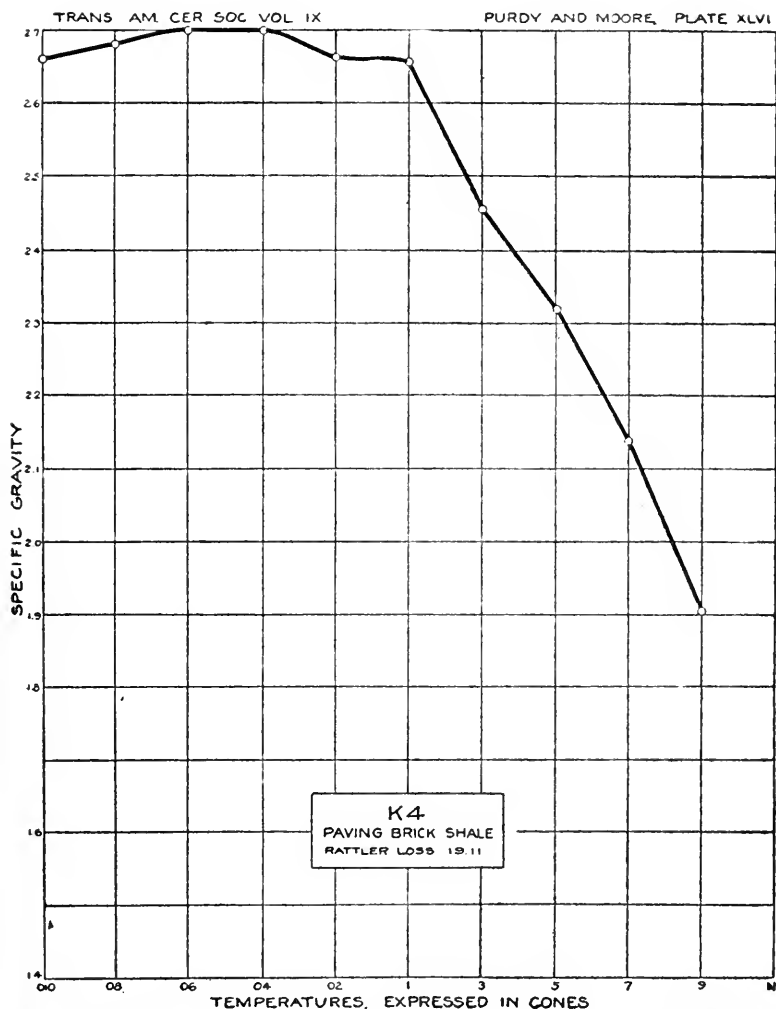temperatures.
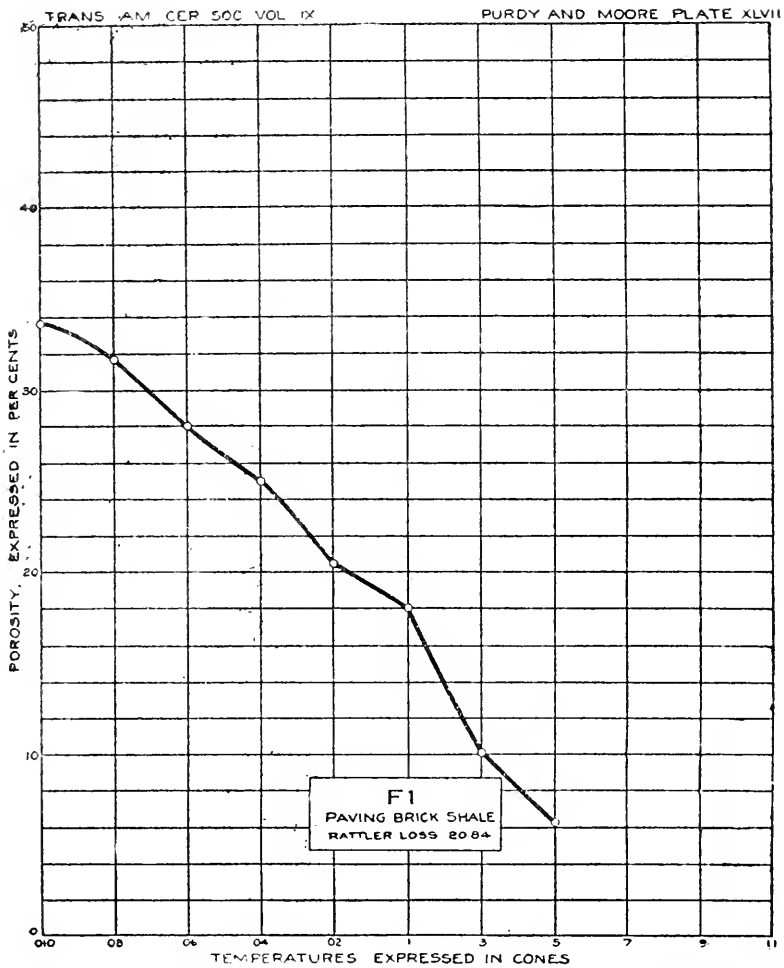
Curve showing changes in specific gravity of clay K 1, at different temperatures.

Curve showing changes in porosity in clay J 2, at different
temperatures.

Curve showing changes in specific gravity of clay J 2, at different temperatures.

Curve showing changes in porosity of clay R 2, at different
temperatures.

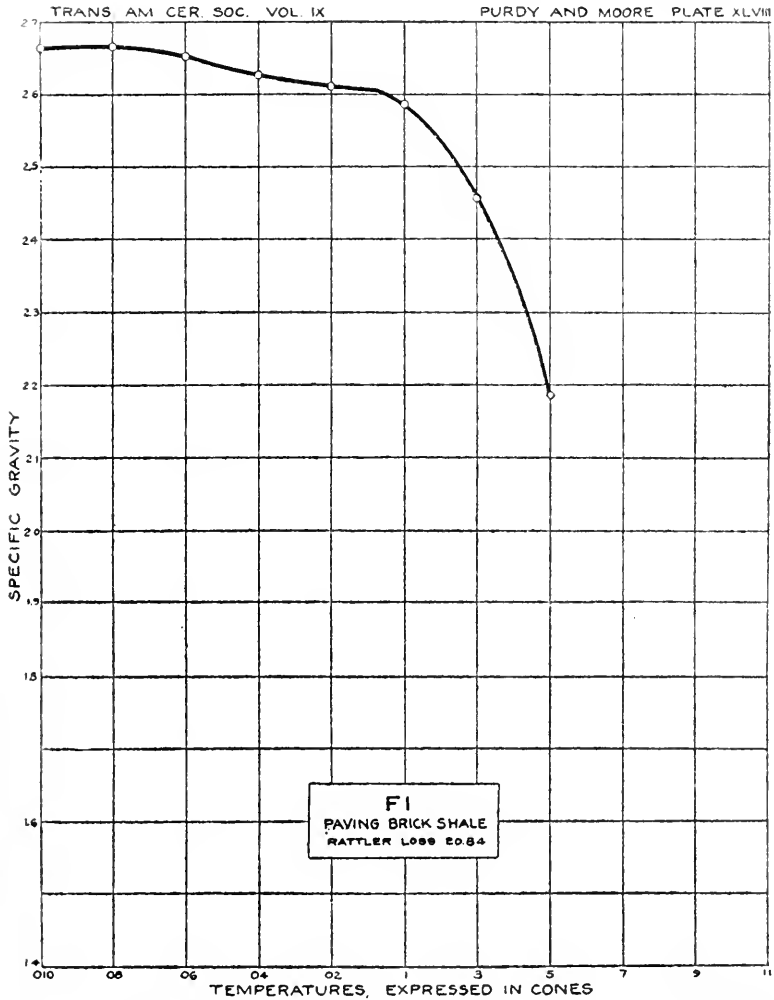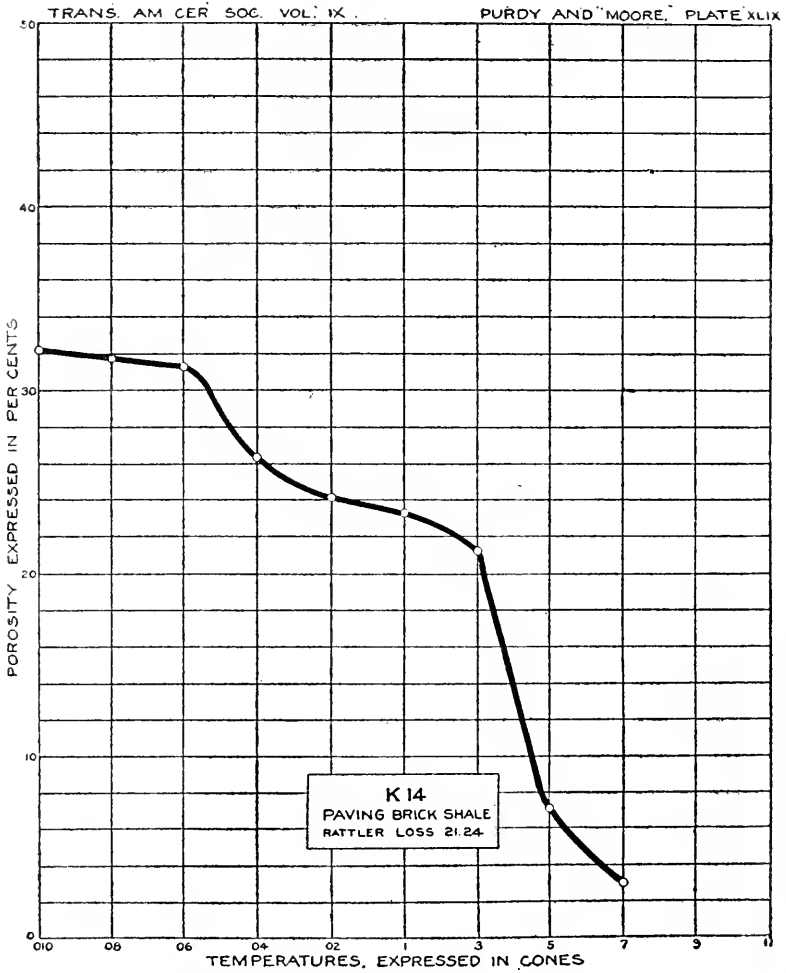Curve showing changes in specific gravity of clay R 2, at various temperatures.

K 4
PAVING BRICK SHALE
RATTLER LOSS 19.11

POROSITY EXPRESSED IN PER CENTS

TEMPERATURES. EXPRESSED IN CONES

Curve showing changes in porosity of clay K 4, at different
temperatures.

Curve showing changes in specific gravity of clay K 4, at different temperatures.
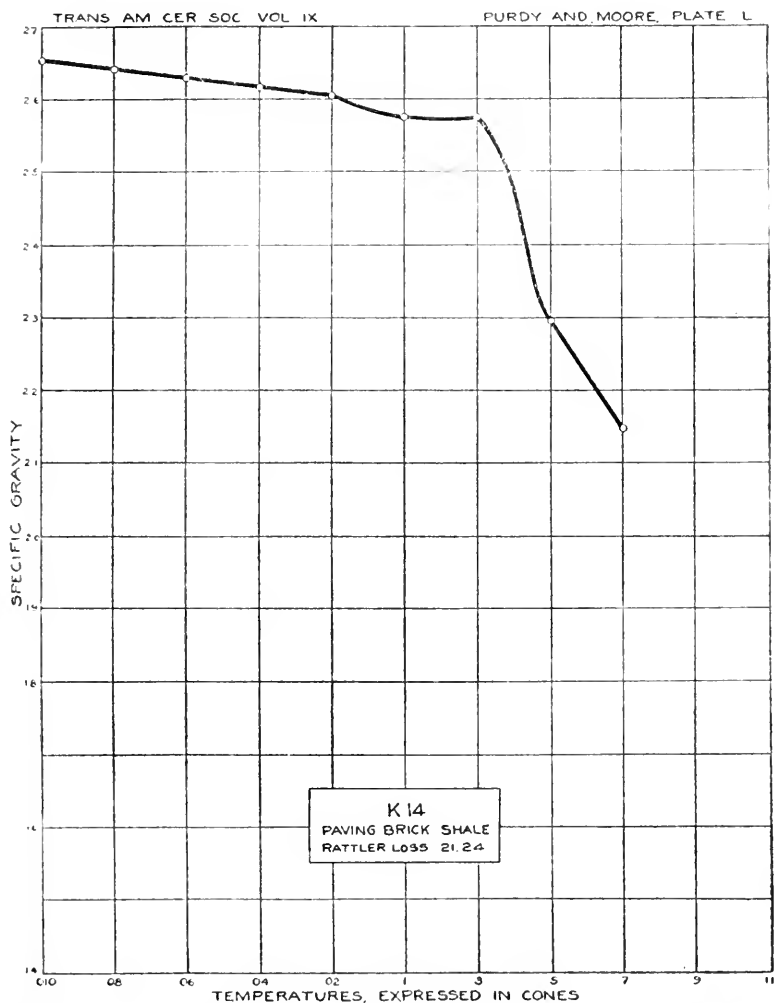
Curve showing changes in porosity of clay F 1, at different temperatures.

Curve showing changes in specific gravity of clay F 1, at different temperatures.

K 14
PAVING BRICK SHALE
RATTLER LOSS 21.24

POROSITY EXPRESSED IN PER CENTS

TEMPERATURES, EXPRESSED IN CONES

Curve showing changes in porosity in clay K 14, at different
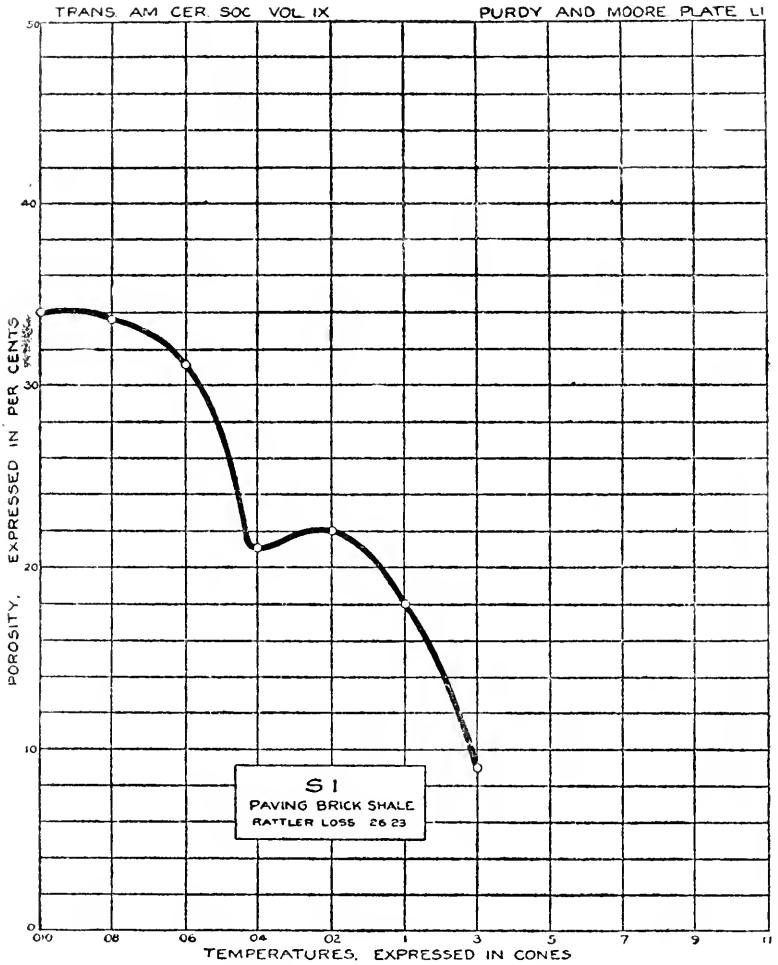temperatures.

Curve showing changes in specific gravity of clay K 14, at different temperatures.
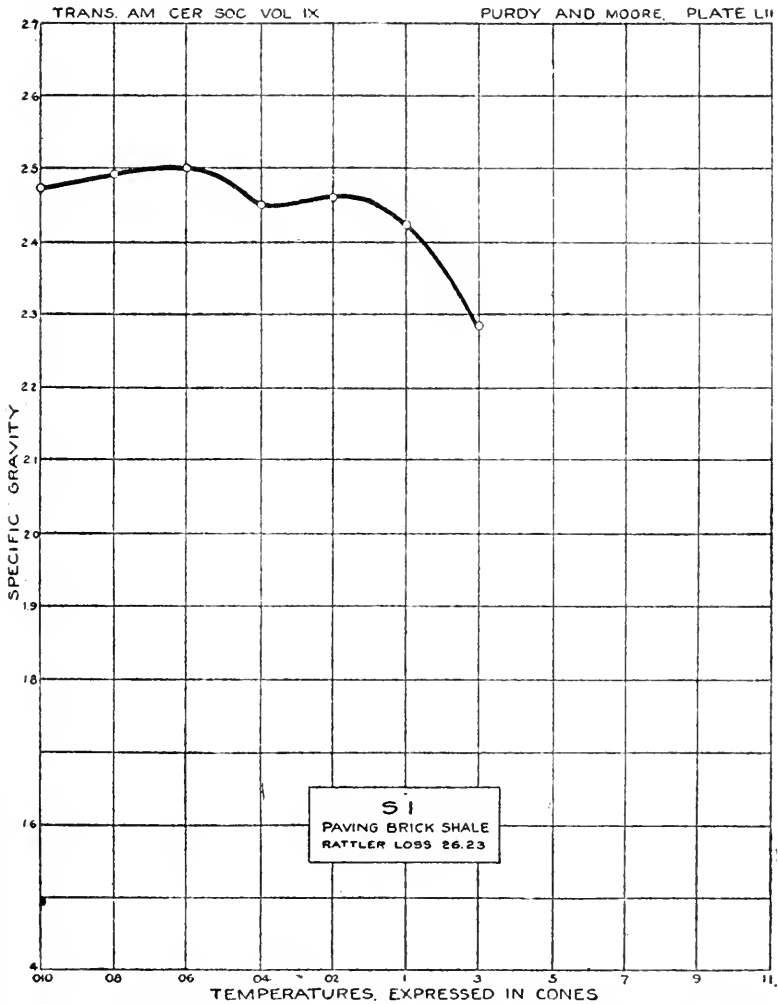
Curve showing changes in porosity in clay S 1, at different
temperatures.

Curve showing changes in specific gravity of clay S 1, at different temperatures.

The chemical composition of the above clays are as follows:[1]

Sam. No.	Mois-ture	Vol'til' matter	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	KNaO	FeO	TiO$_2$
R 3	1.06	5.95	58.57	20.40	7.40	0.63	1.37	3.27	....	....
R 2	1.29	4.86	63.41	18.61	5.82	0.41	1.16	3.60	....	....
J II	1.98	6.76	62.70	16.95	8.98	1.19	1.47	3.03	....	....
F 1	2.02	7.72	58.52	15.67	4.99	1.05	1.45	4.42	3.37	0.96
K 1	0.48	6.99	63.36	15.43	1.80	0.93	1.58	3.84	4.02	1.00
K 4	0.51	5.47	64.09	14.16	2.65	1.69	1.64	3.67	3.16	0.89
K 6	0.38	5.88	63.62	16.28	3.02	0.63	1.44	3.10	2.90	0.96
K 3	0.29	7.89	59.34	15.36	3.26	0.76	1.82	4.62	3.84	1.31
K 14	0.51	6.47	64.09	14.16	2.65	1.69	1.64	3.67	3.16	0.89

Calculated into molecular ratios, the above analyses reduce to:

Sample Number	CaO	MgO	KNaO	Fe$_2$O$_3$	Al$_2$O$_3$	SiO$_2$	FeO	TiO$_2$
R 3	0.056	0.171	0.209	0.231	1.00	4.88	.....	.....
R 2	0.040	0.159	0.253	0.199	1.00	5.79	.....	.....
J II	0.125	0.221	0.234	0.378	1.00	6.29	.....	.....
F 1	0.122	0.236	0.359	0.203	1.00	6.35	0.305	0.078
K 1	0.110	0.261	0.290	0.074	1.00	6.98	0.369	0.083
K 4	0.042	0.282	0.277	0.181	1.00	5.78	0.156	0.060
K 6	0.070	0.225	0.325	0.118	1.00	6.64	0.252	0.075
K 3	0.090	0.302	0.356	0.135	1.00	6.57	0.354	0.108
K 14	0.217	0.295	0.311	0.119	1.00	7.69	0.309	0.080

The mechanical analyses[2] of the above clays are as follows:

Sample Number	L'ger than 1 m. m.	1-0.1 m. m.	0.1-0.01 m. m.	0 01-0.001 m m.	0.001-0 m. m.	Total	Surface factor by Purdy's method
R 3	11.695	6.302	52.902	21.605	11.791	104.295	290.67
K 1	7.276	6.534	56.078	24.861	9.766	104.515	256.476
K 4	1.402	1.744	48.875	29.416	22.242	103.68	513.508
K 6	1.241	1.832	65.836	25.984	7.772	102.666	220.596
K 3	1.500	2.413	57.155	25.148	13.968	100.18	341.155
K 14	14.331	6.311	42.751	25.035	9.672	98.999	254.354

[1]Analyses by Professor S. W. Parr, University of Illinois.
[2]By J. F. Krehbiel and J. K. Moore.

The rattler losses as determined on the commercial product of these clays,[1] obtained direct from the factories, are given in the following table. b. c. d. and e. signify respectively, Soft-burned, No. 2 or "Alley" grade, No. 1 Paver, and Over-burned.

Sample Number	Total Rattler Loss at end of				Absorption in per cent	Tranverse Modulus of Rupture
	600 Revolu.	1200 Revolu	1800 Revolu.			
R 3	8.74	12.22	14.80	. . . . .	1.27	2800
R 2	9.76	14.78	18.61	. . . . .	2.21	2505
	450 Revolu.	900 Revolu.	1350 Revolu.	1800 Revolu.		
J II	8.43	12.25	15.11	17.14	2.315	2220
F 1 b	19.32	29.31	38.88	46.67	13.2	. . . .
c	12.70	19.81	25.08	30.15	4.8	1700
d	9.13	13.89	17.64	20.84	2.8	1980
e	9.75	17.20	23.22	28.35	1.7	1670
K 1 b	17.37	28.56	39.96	46.06	11.2	. . . .
c	13.28	21.46	28.20	33.91	6.1	1630
d	8.43	11.50	14.08	15.82	0.9	2535
e	9.42	16.15	21.77	26.99	1.2	1420
K 4 b	19.69	30.60	38.17	45.12	12.20	980
c	9.22	14.47	17.00	19.94	5.00	2360
d	9.91	14.18	16.87	19.11	1.16	2250
e	14.83	18.92	broken up		0.60	1890
K 6 b	7.9	13.36	18.20	22.77	. . . . .	. . . .
c	7.5	11.68	15.40	18.33	. . . . .	. . . .
d	5.84	9.06	11.58	13.25	. . . . .	. . . .
e	8.42	12.85	16.52	20.32	. . . . .	. . . .
K 3 b	18.54	29.53	38.35	46.21	10.0	995
c	11.34	17.45	21.23	24.61	3.5	2100
d	12.69	19.01	22.49	24.89	1.05	2350
e	11.07	18.58	23.11	26.42	0.70	2700
K 14 d	8.35	13.35	17.30	20.79	4.218	1617

[1] By Professor A. N. Talbot, University of Illinois.

The writers confess their inability to correlate the chemical and mechanical analyses of these clays with their pyro-chemical behavior or their rattler loss, but since they represent the most commonly accepted facts which have been collected heretofore in the study of paving brick clays, they are here recorded for reference.

COMMON OR BUILDING BRICK SHALES.

Typical porosity and specific gravity curves of this class of clays are given in the following six charts.

The striking difference between these and the paving brick shales is apparent. Earlier vitrification, irregularity in decrease of porosity and specific gravity, apparently larger quantity of vesicular glass formed within the mass, or at least a more notable bloating, due to volatilization of certain constituents, probably the soluble and adsorbed salts, are the distinguishing features of this class.

Sufficient evidence is at hand to warrant the statement that any clay which vitrifies to a porosity of 2 or 3 per cent. before cone 5 is reached in the heat-treatment prescribed in this method of burning test pieces, will be too brittle for use as paving brick material, no matter how little vesicular structure is developed. The fact is, however, that it will be a rare case in which vesicular structure is not strongly developed, if the clay shows an early and rapid rate of vitrification.

The use of the comparative terms "early" and "rapid" in reference to this type of clays in contrast to their relative use in regard to fire clays, is best illustrated by reference to the curves.

While the writers admit that the evidence here presented is too meagre to permit of a complete or satisfactory plan of classification, they do feel that it is sufficient to indicate that a classification on the basis suggested is more rational than any other heretofore presented.
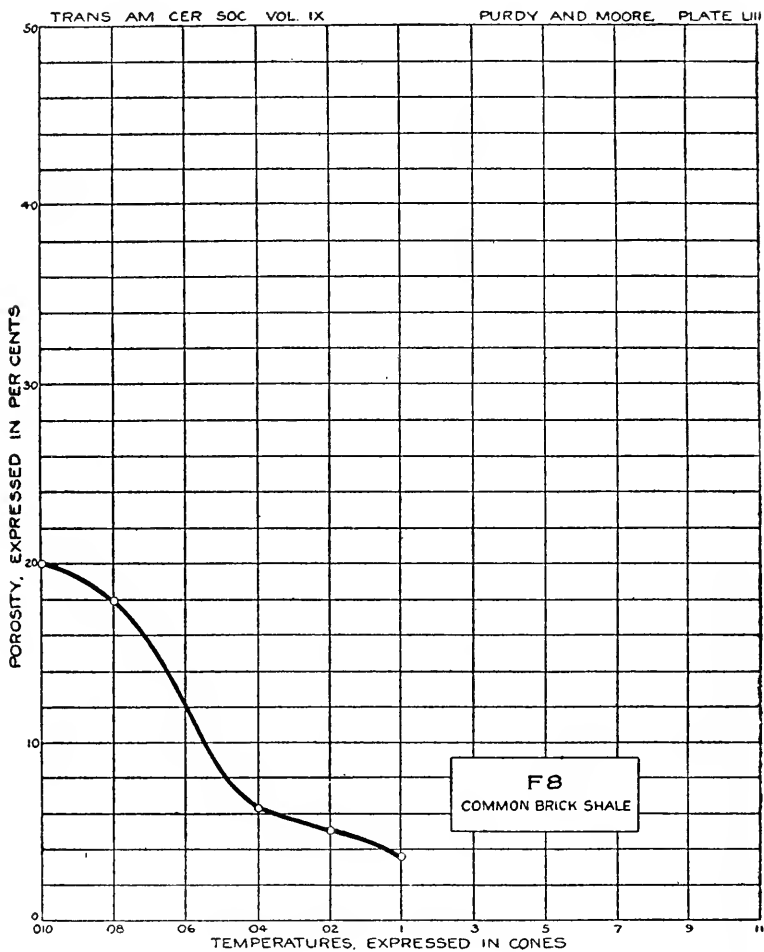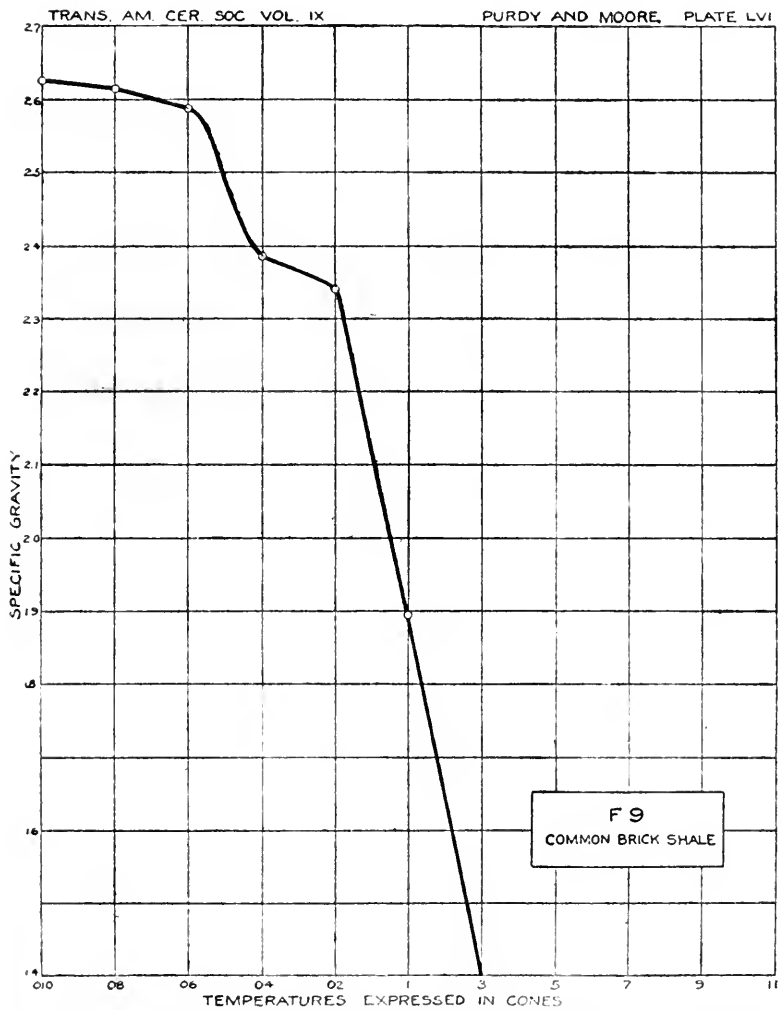
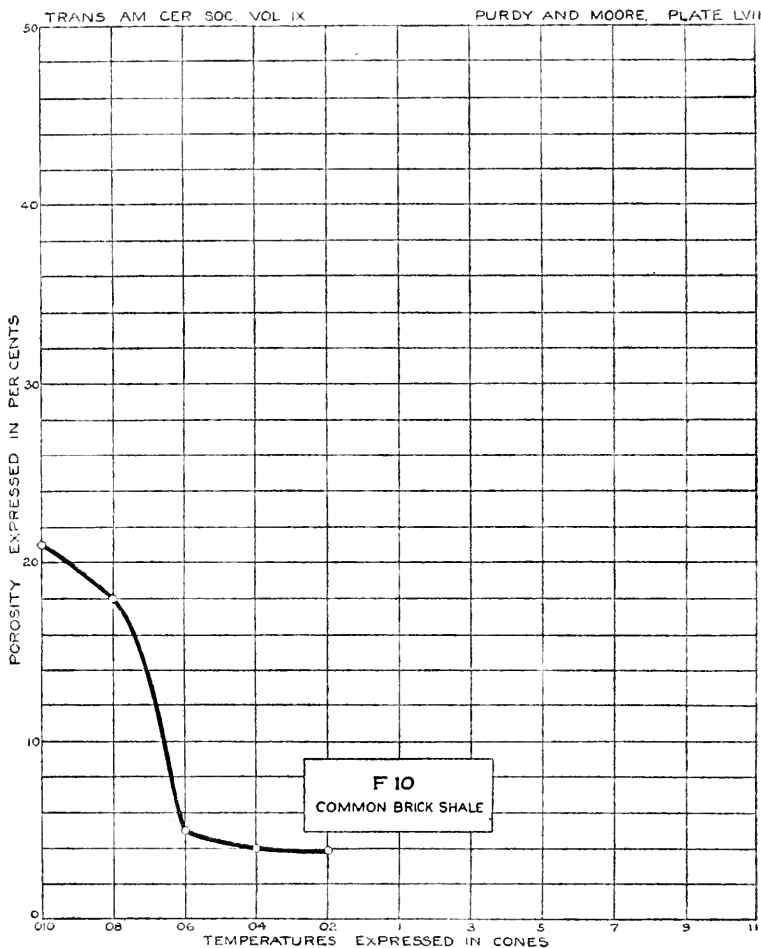Curve showing changes in porosity of clay F 8, at different temperatures.
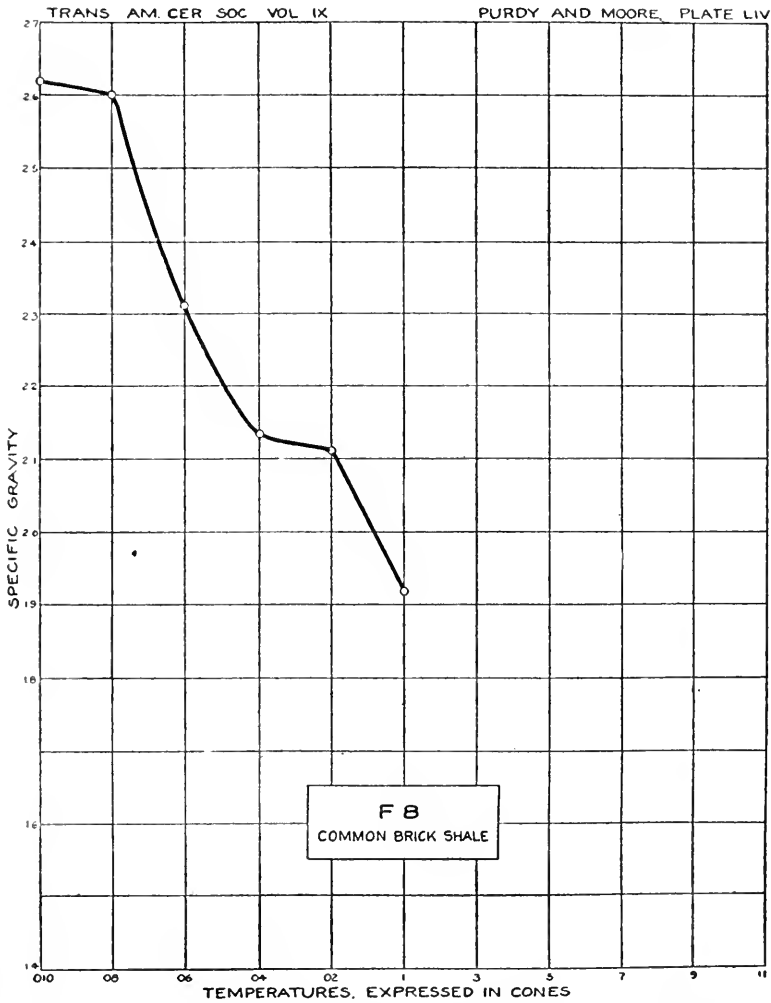
Curve showing changes in specific gravity of clay F 8, at different temperatures.
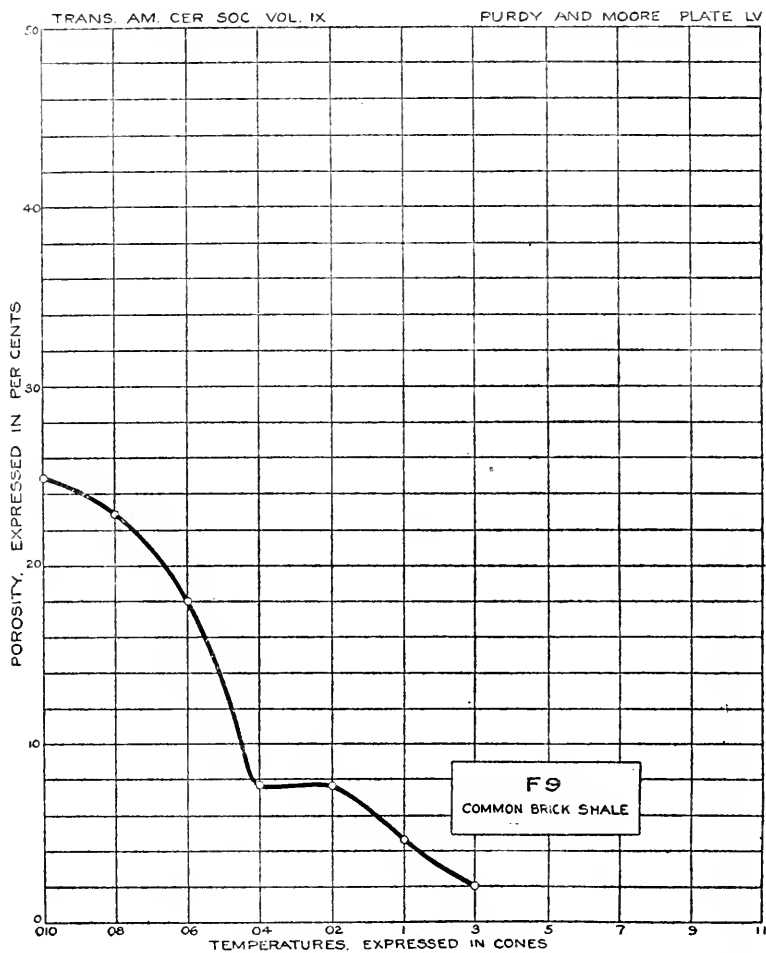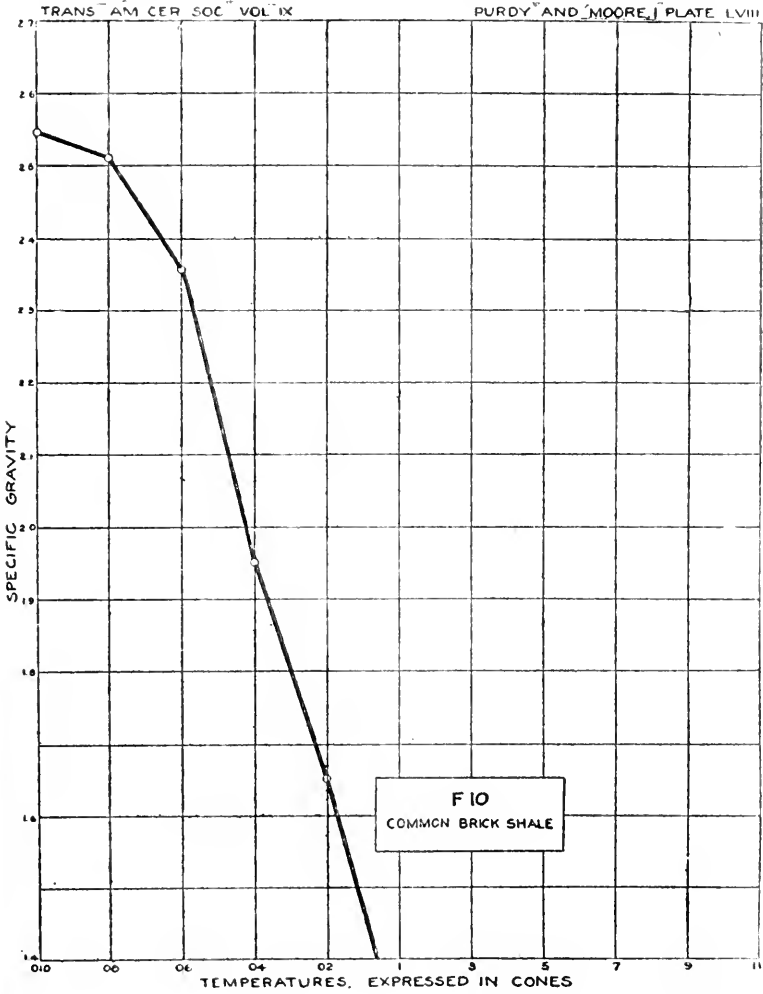
Curve showing changes in porosity of clay F 9, at different
temperatures.

Curve showing changes in specific gravity of clay F 9, at different temperatures.

Curve showing changes in porosity of clay No. F 10, at different temperatures.

Curve showing changes in specific gravity of clay F 10, at different temperatures.

COMPARATIVE THERMO-PHYSICAL CHANGES.

The following curves are presented to show the comparative rate at which the three most important thermophysical changes take place.

A full explanation of the method of plotting these curves has been given earlier in the text.

The volume, porosity, and specific gravity of the dry unfired brick being considered as a basis, and plotted in the datum line, the co-ordinate points of increase or decrease of these same factors in the burned brick are plotted as shown on the curves.
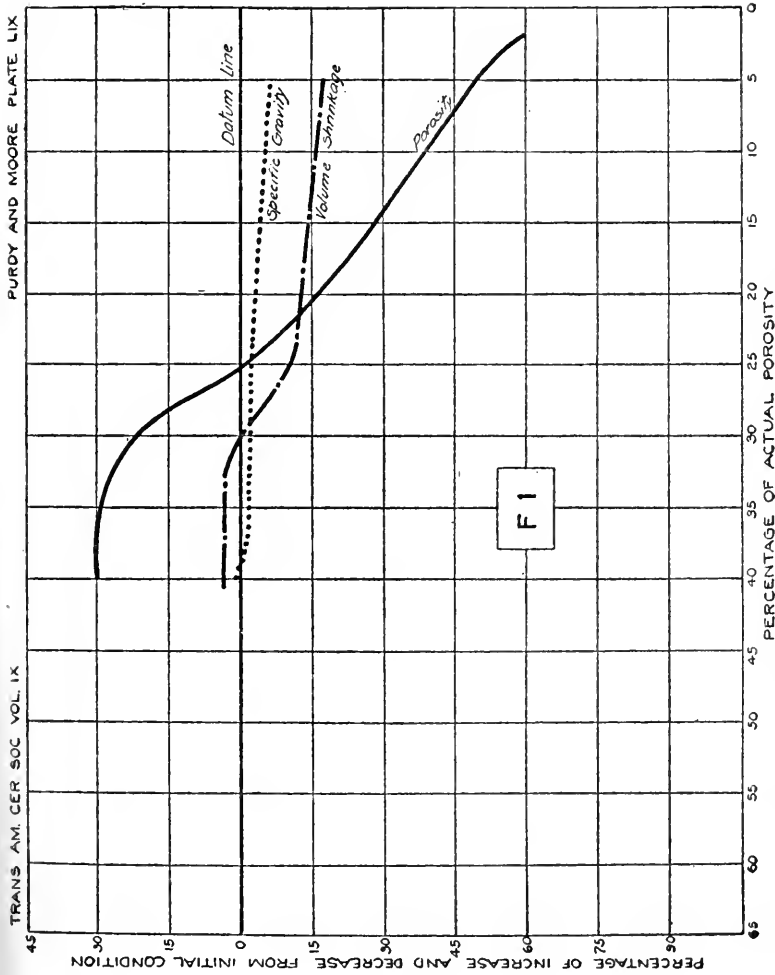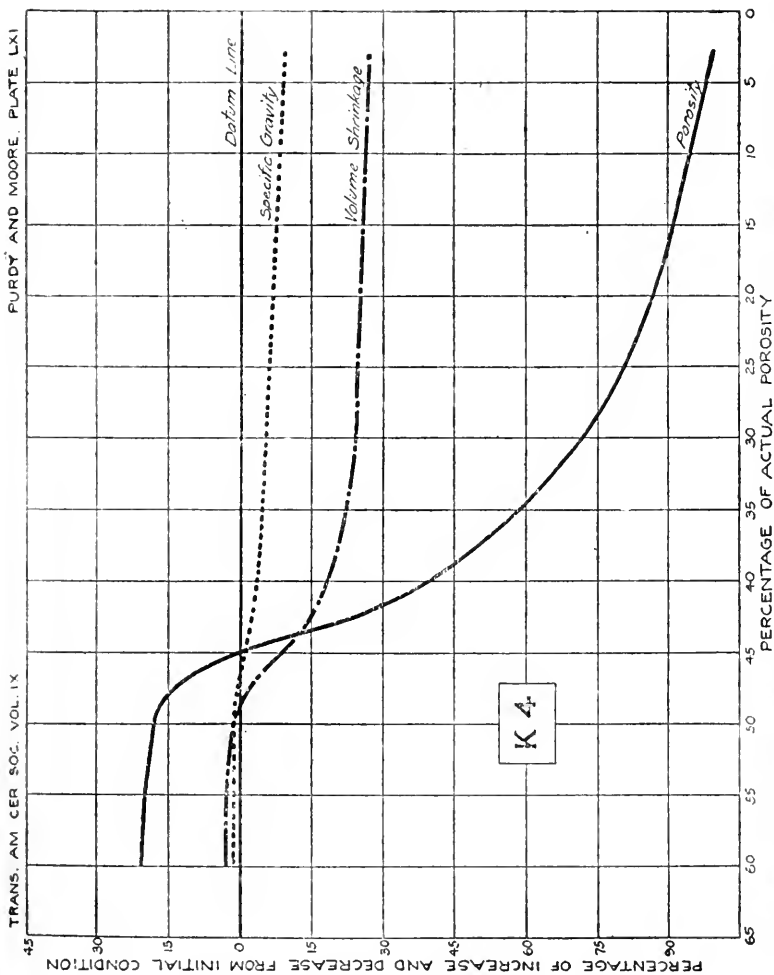
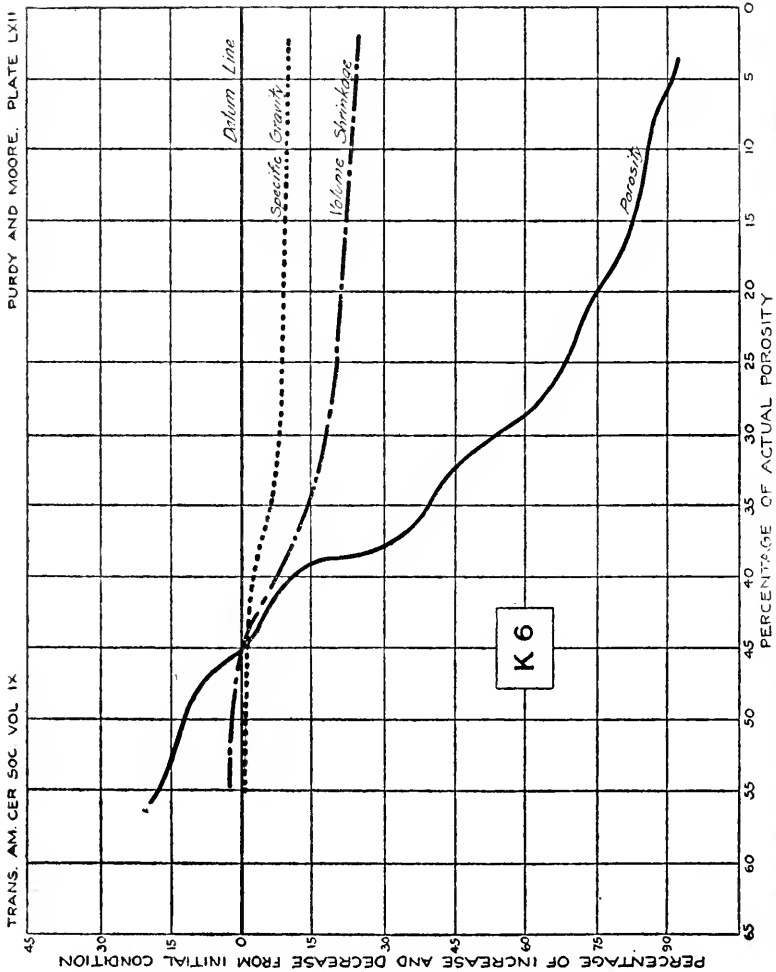Curves showing properties of clay F 1, at various stages of burning, compared to its properties in the unburnt condition as a datum.
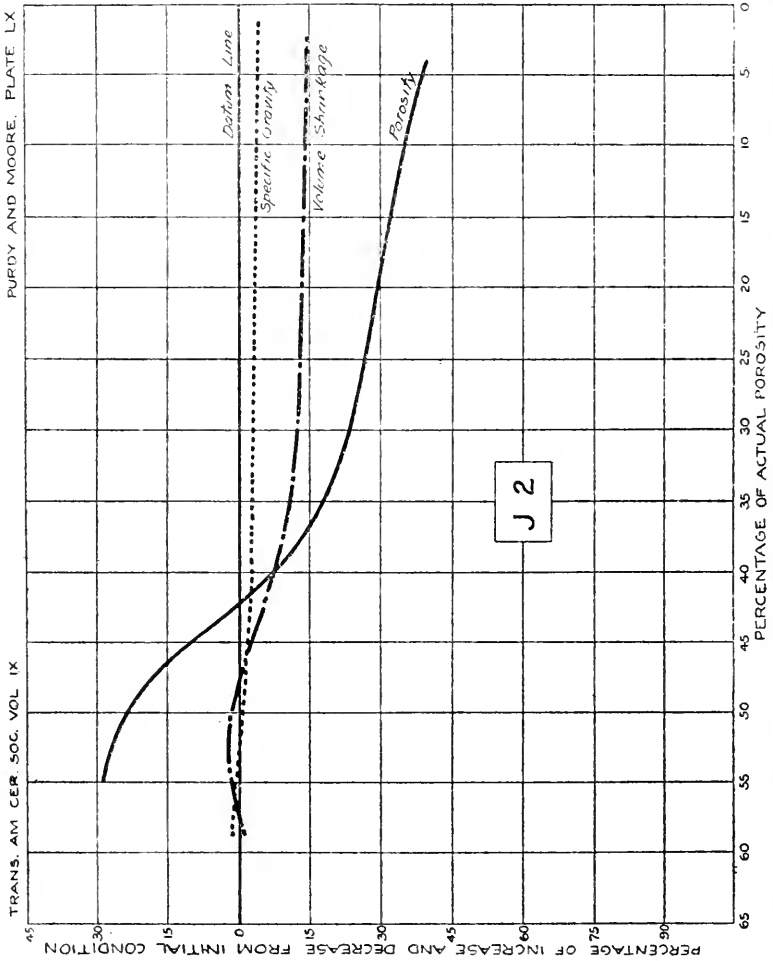
Curves showing properties of clay J 2, at various stages of burning, compared to its properties in the unburnt condition as a datum.

Curves **showing** properties of clay K 4, at various stages of burning, compared to its properties in the unburnt condition as a datum.
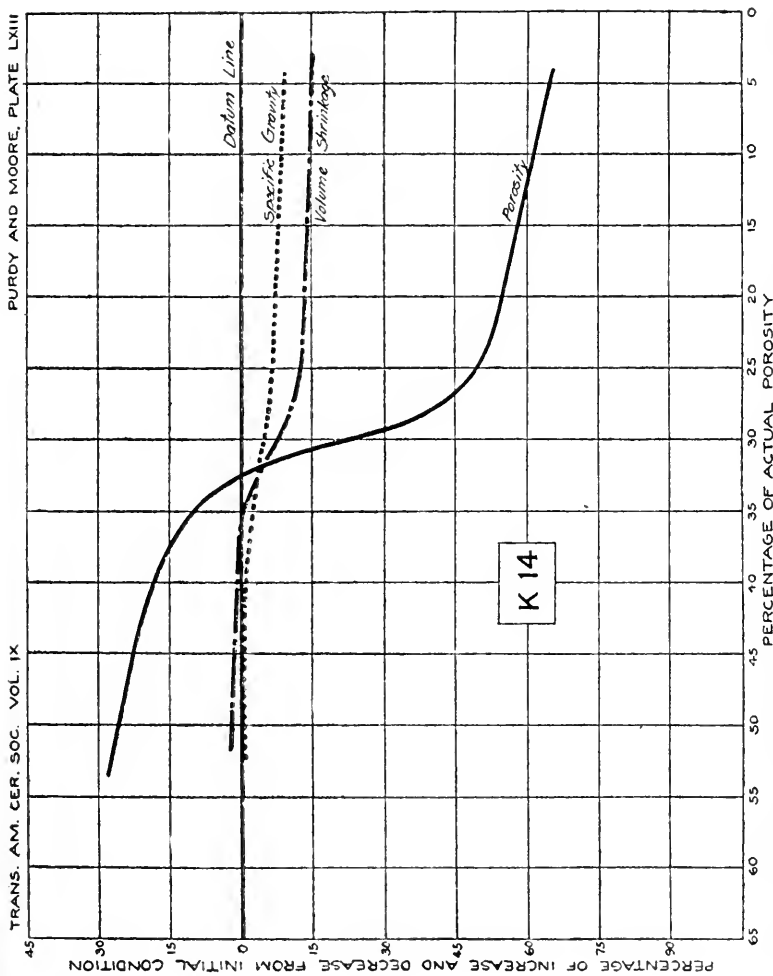
Curves showing properties of clay K 6, at various stages of burning, compared to its properties in the unburnt condition as a datum.
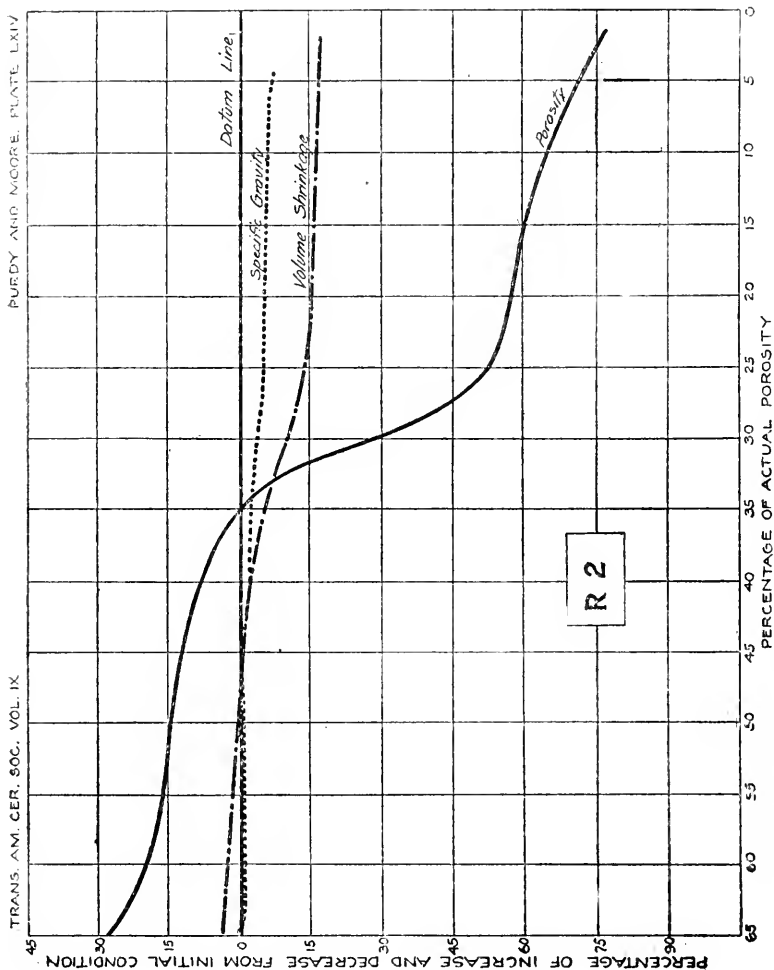
Curve showing properties of clay K 14, at various stages of burning, compared to its properties in the unburnt condition as a datum.

Curves showing properties of clay R 2, at various stages of burning, compared to its properties in the unburnt condition as a datum.

Curves showing properties of clay S 1, at various stages of burning, compared to its properties in the unburnt condition as a datum.
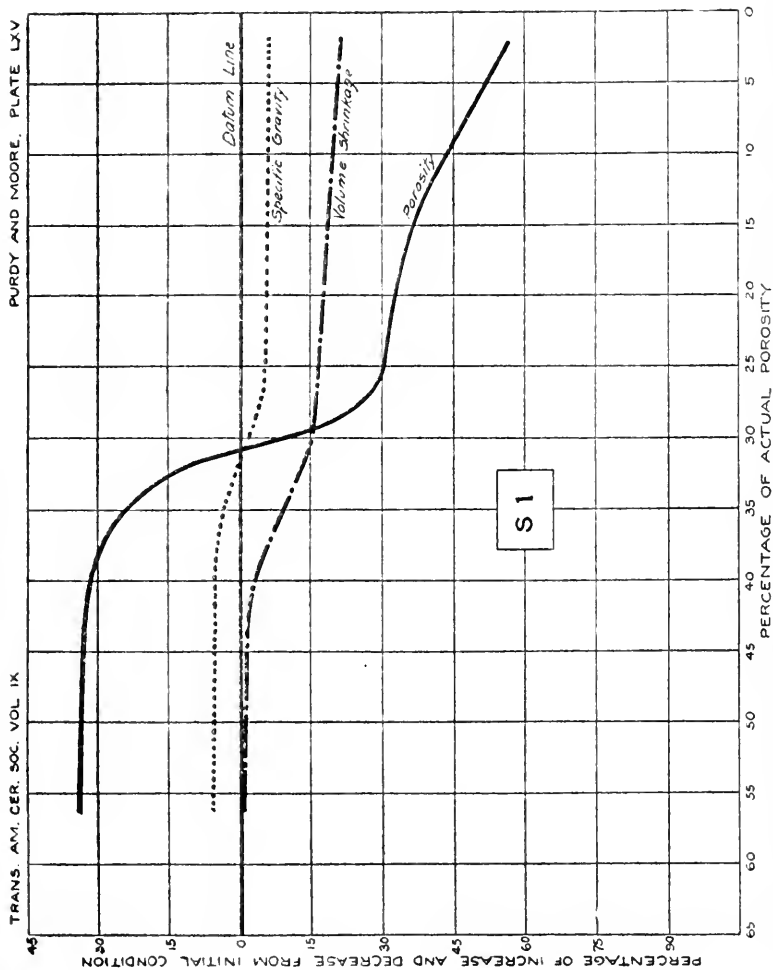
ULTIMATE FUSIBILITY OF CLAYS.

Ludwig,[1] by the application of known physico-chemi-cal laws, deduced a scheme by which he was able to predict the fusibility of clays. H. J. Robertson,[2] discussing Ludwig's results quite fully, concurred in his general conclusions. The Ludwig scheme as presented by Robertson was followed in the construction of the chart on page 313.

The Seger cone molecular formulæ were reduced to $Al_2O_3=1$. The molecular equivalents of silica were plotted on the ordinate, and the molecular equivalents of RO fluxes on the abscissae. It will be noted that in no case does the molecular ratio of Al_2O_3 to SiO_2 exceed 1:10. This being the ratio of Al_2O_3 to SiO_2 in cones 5-25, their co-ordinate position is located on a horizontal line drawn from the ordinate 10. Having the chemical composition of clays of various kinds, the chart was prepared and the co-ordinate position of each clay plotted.

The accuracy with which the fusibility of a clay can be thus ascertained, is shown by the fact that in nearly every case, the result reached by plotting the molecular ratios checked with that reached by the actual fusibility test, regardless of the purity or grade of the clay tested.

The labor of making the analyses and calculating the molecular formulæ, and the chances of disagreement between the plotted and actual fusibility, places the Ludwig scheme at a serious disadvantage. Inasmuch as direct tests afford an easier and surer method, Ludwig's indirect test will hardly come into general use. The Ludwig scheme, however, has been of great value in that it has established the fact that clays, although a heterogeneous mixture of minerals, do, as a rule, obey definite laws in fusion.

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[1]Tonindustrie Zeitung No. 63, 1904, abstracted by Prof. Bleininger, Vol. VII, p. 275, A. C. S. Trans.
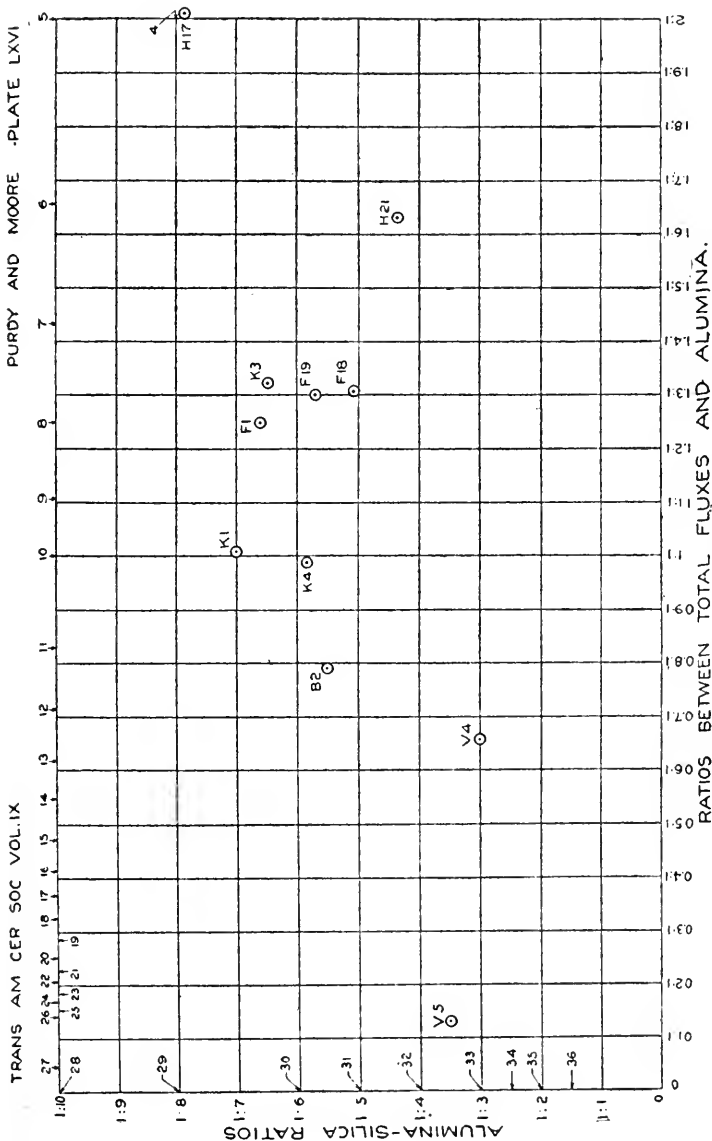
[2]Brick, Vol. XXV, No. 2, 1906, p. 62.

Chart showing relation between the fusion points of various clays calculated by the system of Ludwig, and their observed fusion point.

CONCLUSIONS.

The writers have attempted to indicate the thermo-chemical and physical changes that take place in the burning of clay wares. Some effort has been made to show the causes of the various phenomena noted, but in the main, because of the lack of data, they have been reluctant to advance explanations with any degree of positiveness. It is believed, however, that by means of the method of study here presented, the following facts in regard to a clay can be established :

1st. Exact industrial possibilities.

2nd. Factor of safety to (a) vitrification range, (b) fusion range, (c) deformation.

3rd. That while thermo-chemical and physical changes follow definite laws, they cannot be foretold by any analysis of the primary causes (physical properties of the unfired clay) now known.

In conclusion, the writers desire to express their appreciation of the kindness of Dr. H. Foster Bain, Director of the State Geological Survey of Illinois, in permitting the use of considerable data collected by the Survey, and also of Professor C. W. Rolfe, Director of the Ceramic Department of the University of Illinois, and the University officials, in liberally supporting the researches that made this presentation possible.

The chemical analyses given in this paper were made by Mr. David Kline and Dean Burns under the direction of Prof. S. W. Parr.

DISCUSSION.*

Mr. Yates: Were these various tests burned under the same conditions—that is, was the temperature of the kiln uniform?

Mr. Moore: These clays were placed all in the same kiln, at the same time, in saggars, and were burned in the

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*This paper was not read in its entirety, but was abstracted and presented in connection with the curves by Mr. Moore. Some of the discussion would probably not have taken place had the paper been read in full.

same operation. Our kiln melts the same cone at the top as at the bottom, so it is certain that we get a uniform distribution of heat.

Mr. Yates: That being the case, isn't your conclusion that the common brick shale, whose curve fell so quickly, is not suitable for paving brick purposes unwarranted? Under the same conditions of firing, these common brick shales would not stand the temperature, but if fired slower, how do you know that they might not have made as good or tougher brick than the shales whose curves descend more gradually.

Mr. Purdy: Mr. Moore has covered the ground, I believe, in a thorough manner; but I wish to bring out a little more emphatically the difference between the No. 1 and No. 2 fireclays. The No. 1 fireclays, (indicating plates IX-XVIII) you will notice, vitrify very slowly. The No. 2 fireclays have an early vitrification, but from there on, they have a very slow fusion rate. They vitrify under stoneware or facebrick heat-treatment, and could be used for either of those purposes. But their actual fusion points agree closely with those of the No. 1 fireclays, and the chemical analysis also agrees in many ways with that of the No. 1 fireclays. The only means of differentiation is in the plotting of their vitrification phenomena in these curves, and noting the remarkable variation which they show. In the case of what we have called No. 3 fireclays, the vitrification is not only more rapid, but the actual fusion point is also considerably lower. A paper was read by Mr. Bleininger on physical chemistry yesterday, and I noted halts in his curves, as shown in these. There is a problem there, for the physical chemists to solve. I feel assured that when they can give an explanation for that halting in the porosity curve (and the same is noted in the specific gravity curve), it will throw a great light on our methods of determining the possible value of the clay. This work which we are presenting in this paper is, perhaps, a crude introduction to the chemical-physical method of studying our most common clay working operations.

In the description of the microscopic slides Mr. Wege-
mann stated that the iron had not discolored the glass,
until after cone nine had been reached. That is equivalent
to saying that the iron had not operated as a flux, even at
cone nine. We have many of us been of the opinion that
iron was one of the most active fluxes in the scale, and we
are not yet ready to give up that opinion; but by examina-
tion of the specific gravity curves and microscopic slides,
we must admit that the iron seems not to enter into active
fluxing action. At any rate, the glass did not take the iron
into solution and the iron had not probably fluxed the clay
particles to any great extent, for the glass would take it up
before the clay particles would.

I would like to call your attention to the rattler losses
placed on the plates of the paving brick shales, numbers 35
to 52. Observe plate XXXV showing a rattler loss of 13.25
and plate LI showing 26.23. Observe the relative changes
in porosity and specific gravity in conjunction with the
rattler loss. Mr. Moore emphasized the fact that this de-
crease in specific gravity was due to the formation of glass.
We know that when a glass is first formed, whether in the
glass pot or in glazes, that there is a boiling up or evolution
of gas. This is especially noticeable when burned rapidly.
When burned slowly, the glass is not boiled up so much,
but is still vesicular in structure; that is, it contains small
blibs or sealed cavities into which water from the outside
could not penetrate.

In Plates LIX to LXV, the datum line represents the
measurements obtained on the unburnt clay. The figures
above show the increase of porosity or specific gravity or
volume over these properties of the raw clay, and the fig-
ures below that datum line show the decrease of these same
properties below that of the raw clay. Thus we see that
samples drawn at cone 010 generally showed actually
greater porosity, greater real specific gravity and greater
volume than the raw material showed, while samples
drawn at higher temperatures showed these properties, one
or all, to be about the same as the initial measurements

and still higher temperatures showed marked falling off in all three sets of properties. I do not pretend to understand all the phenomena brought to light in this study, for I have not yet had the assistance of one well grounded in physical chemistry.

In the plates LIII to LVIII, are shown brick made of common shale. There have been engineers who have insisted on the specific gravity test, as a test of the wearing qualities of paving brick. We have found that when the *true* specific gravity, that is, the specific gravity of the mass as a whole, is taken, it gives a good index of the strength of the product. This is well shown in these charts. The specific gravity cannot be taken direct: It must be taken in connection with the specific gravity of the raw clay, in order to get a comparison between the two. What does the specific gravity tell you? It tells you the extent to which this glass matrix, which Mr. Wegemann has described, has become blibbed or foamy. The more foamy it has become, the weaker your clay will be and the heavier will be its rattler losses.

Mr. Yates: Do I understand that these globules of glass are separate particles in the body of the brick, or are they assimilated with the body of the brick?

Mr. Purdy: A study of all the clays in microscopic section shows similar phenomena. There will be a particle of quartz, a particle of some other amorphous substance, a particle of fused glass, you might say, in a row, like the cross section of a sausage, mixed hit or miss. There is no regularity about it; it is not stratified.

Mr. Binns: I want to ask Mr. Purdy, in connection with that iron fusion, where the hematite crystals are seen appearing, isn't what followed evidence of combination of the iron with the silica?
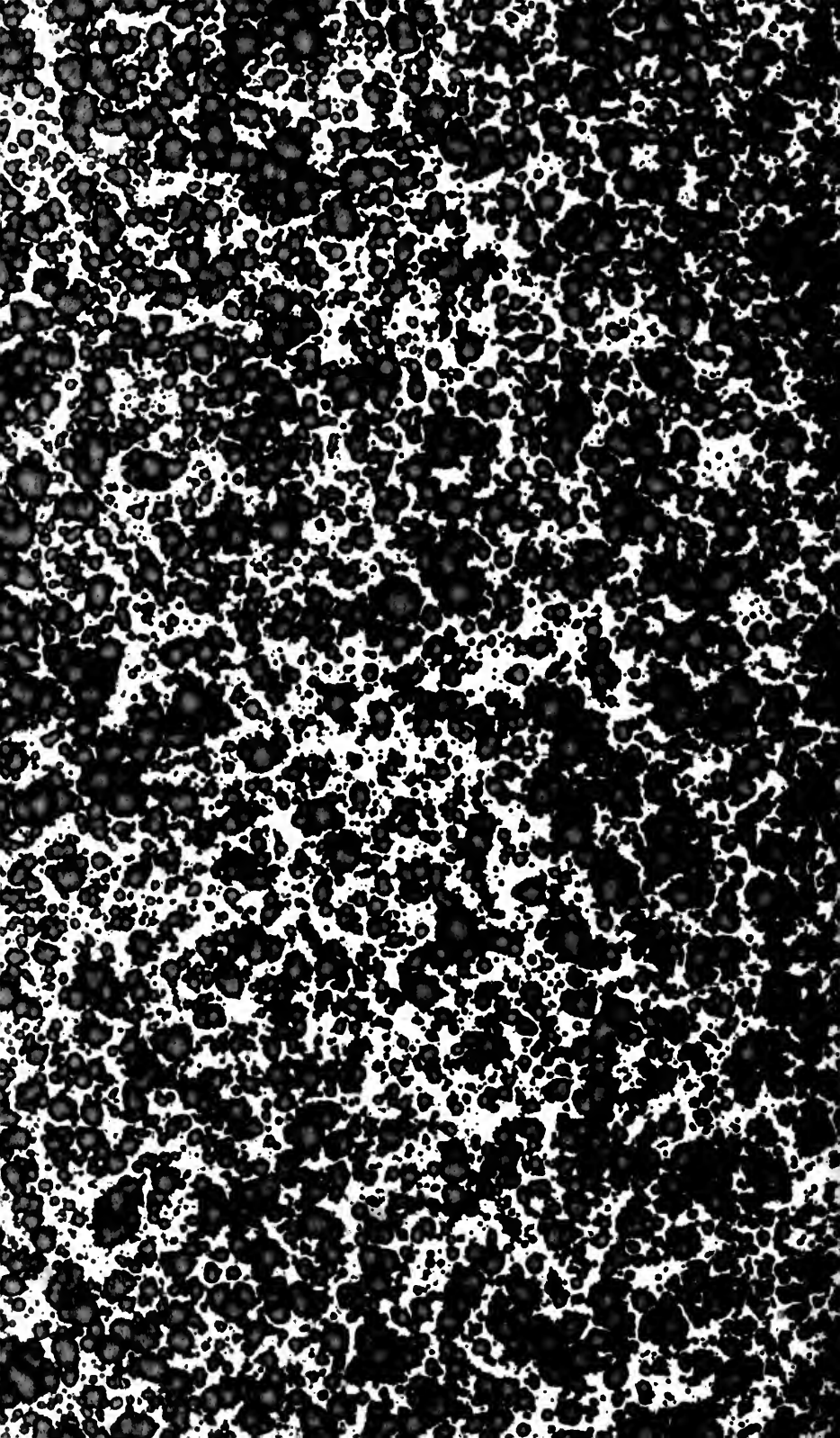
Mr. Purdy: No.

Mr. Binns: Was it reduced?

Mr. Purdy: Yes, but in many instances the hematite crystals were formed even where there was every appear-

ance of wholly reducing conditions. The increase of hema-
tite crystals progressed through the red or ferric state into
the black or ferrous brick.

I want to draw attention to the fact that some of these
fireclays had so little flux that it was not noted in the
chemical analysis, the alumina, silica, titanium, and water
being the only constituents reported. What is there in
such a clay which forms this glass? What is it in the
shales? There is a nice little problem in your adsorption
theory. We are beginning to put two and two together,
but we are not quite yet willing to add them.