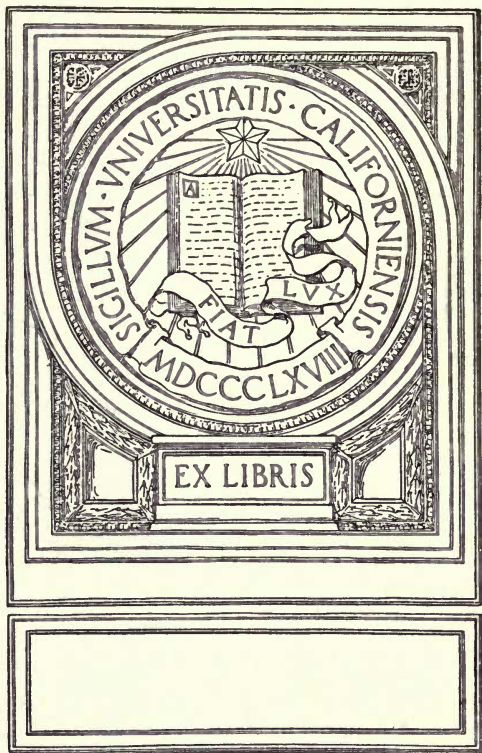


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C. W. ROLFE, Director

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## THE INFLUENCE OF FLUXES AND NON-FLUXES UPON THE CHANGE IN THE POROSITY AND THE SPECIFIC GRAVITY OF SOME CLAYS.

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By A. V. BLEININGER and J. K. MOORE

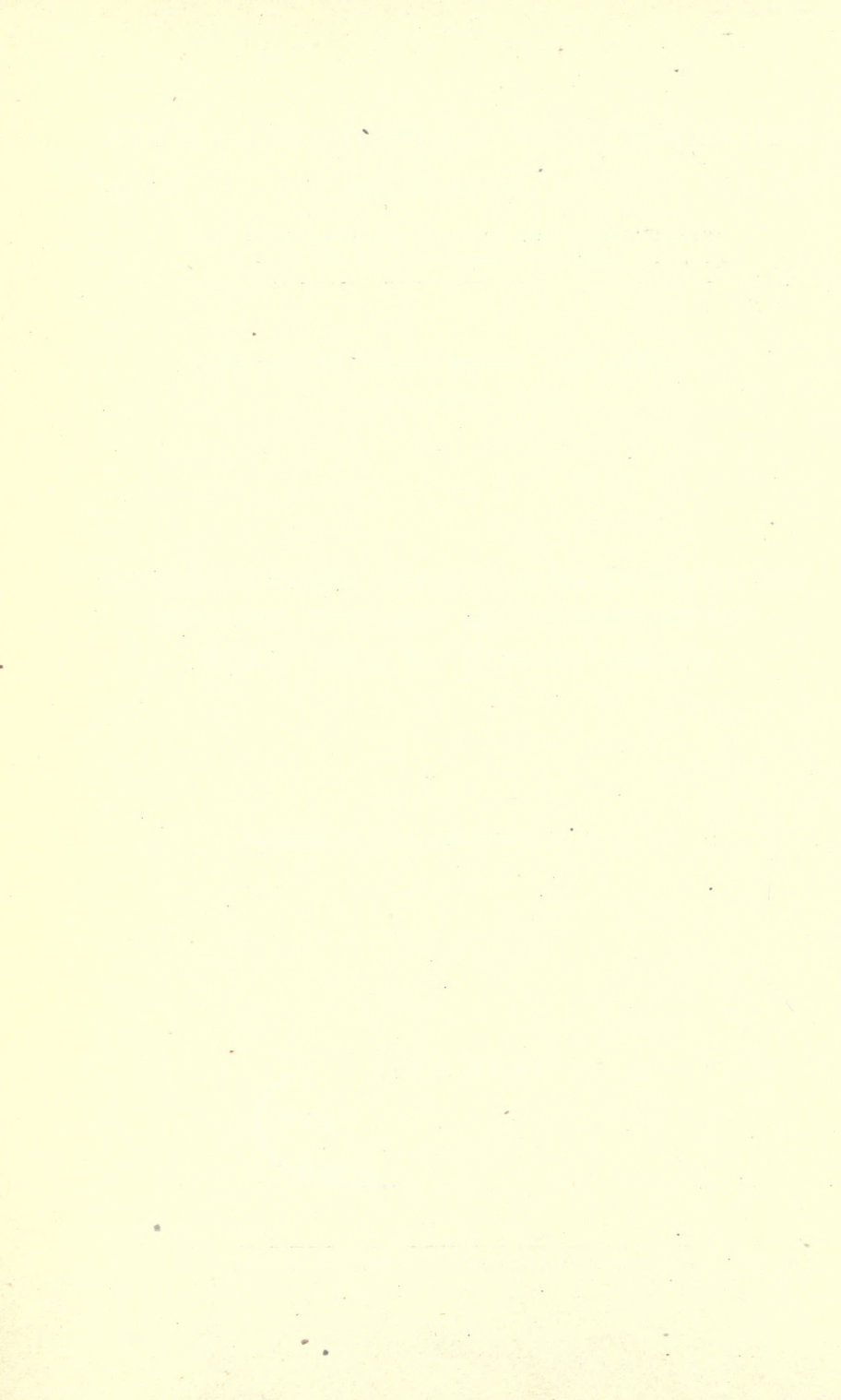
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# THE INFLUENCE OF FLUXES AND NON-FLUXES UPON THE CHANGE IN THE POROSITY AND THE SPECIFIC GRAVITY OF SOME CLAYS.

BY

A. V. BLEININGER AND J. K. MOORE, Champaign, Ill.

Vitrification may be said to be partial fusion. When speaking of clays the progress of vitrification is equivalent to progressive, partial fusion of the various mineral constituents, governed by the mineral constitution of the body as a whole, the size of grain and the structure of the ware for which the clay is employed. Complete vitrification ensues when enough clay has been used to fill up the pores originally present. From the practical standpoint this is indicated by the fact that but little water is absorbed by the clay on immersion. Without going fully into the details of the process it may be said that the phenomena of fusion accompany the vitrification of clays.

Fusion considered from the general standpoint of silicates is sharply defined only for some definite minerals; even in many silicates it is a more or less gradual transition from the solid to the semi-liquid or liquid condition, and therefore, in a heterogeneous rock, like clay, even though all of its constituents were reduced to uniform, extreme fineness, fusion must, in the nature of the case, cover a considerable temperature interval.

From the practical standpoint, therefore, vitrification may be followed by determining the porosities at different temperatures, just as Prof. Purdy has done in his valuable contribution in Vol. IX of the Transactions of this Society.

In addition, two phenomena of fusion demand our attention. These are closely related and are: Change in molecular volume and transference of heat. In nearly all silicates the volume is increased on fusion or, in other

words, the density is decreased. This increase in volume is intimately connected with the fact that the amorphous or fused condition represents a greater energy potential than the crystalline state. We find, as a rule, that the amorphous modification of a substance is more soluble and capable of stronger reaction than the anisotropic form. That fusion results in an increased volume has been determined frequently, and in a few cases it was even possible to establish this fact for minerals in the fused, liquid condition. Thus Doelter found the specific gravity of crystalline augite to be 3.3, that of the hot, liquid mass 2.92, and of the solidified glass, 2.92. The so-called coefficient of crystallization, in fact, is determined by the specific gravity of an intermediate stage compared with the specific gravity of the crystal. If  $d_x$  = specific gravity at any stage and  $d_c$  = specific gravity of the crystal,  $d_x \div d_c$  = coefficient of crystallization. E. V. Fedorow has shown that this agrees with the facts.

With reference to the heat of fusion we can say that this is of constant magnitude, and is equal to about 100 gram calories per gram. Fusion is always accompanied by absorption of heat. This is a necessary conclusion, for in fusion, work is always done against the external pressure and the cohesion of the particles, both of which tend to oppose the increase in volume. That the non-crystalline condition corresponds to a higher level of energy may be indirectly shown by experiments such as the determination of the heat of solution. Thus 1 gram of crystalline sodium silicate evolves 457 calories, while the same amorphous substance gives off 486 calories. Similarly, crystalline leucite shows 507, the amorphous substance 533 calories.

From what has been said it follows that crystallization shows the opposite characteristics. On crystallization the volume decreases and heat is given off, thus retarding the cooling of the mass.

The fact that clay bodies decrease in density on vitrification had been realized quite early by Laurent, Brongniart and Rose, and during the last decade has been used



in very exact work by Day and Shepherd, Mellor and others. The rate of change in specific gravity and porosity has been employed in the plotting of density and porosity curves by Berdel in his excellent and extensive work on white ware bodies and, later, by Purdy in his work already cited. Purdy emphasizes the rate of change in porosity and makes use of the specific gravity only for the purpose of determining the porosity which he considers as the criterion for judging the progress of vitrification. He calculates the porosity, expressed in per cent, from clay brickettes burnt at different temperatures and uses the formula:

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

where % P = per cent porosity.

W = wet weight of brickette.

D = dry weight.

S = suspended weight.

The wet weight corresponds to the weight of the brickette after immersion in water, in vacuo.

By plotting the porosities of a clay at different temperatures he obtains a curve which unquestionably indicates the progress and rate of vitrification. Prof. Purdy advocates the use of such curves in clay testing for the purpose of determining the character of a clay, and there is no doubt but that this offers a very convenient and valuable method of testing which deserves general application. The writers make continuous use of the method in carrying on clay tests.

While the porosity curve is of great practical value, yet it seems to the writers that much information in regard to the mechanism of the changes occurring in clay during burning is obtained from the particular study of the changes in specific gravity, that is, the specific gravity curves. In using this method we are simply adopting the means employed by many investigators in following chemi-

cal transformation, as, for instance, by Van't Hoff in his study of plasters, etc.

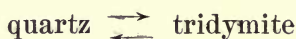
While in many clays and clay bodies the porosity and specific gravity curves are practically parallel, yet it may happen that certain changes occur which are indicated only by the specific gravity curve.

In discussing the density of clays we must clearly distinguish two values of the density which differ according to the method by which the work is carried out. If we take a brickette, weigh it when dry, immerse it in water, in vacuo, and again weigh it suspended in water, we obtain by calculation from the simple formula:

$$\text{Specific gravity} = \frac{\text{Dry weight in air}}{\text{Dry weight in air} - \text{suspended weight}},$$

the specific gravity of the brickette as a whole, including the effect of enclosed pores and other cavities. On the other hand, by crushing and powdering the brickette and using the pycnometer, being careful to exhaust the air from the powdered material and water in the apparatus, we shall have the specific gravity of the burnt clay itself, the effect of the pores and cavities having been eliminated.

In addition to the change in volume brought about by fusion we have other volume transformations caused by so-called inversions, that is, the character of the molecular arrangement of many compounds suffers an alteration. The best known instance of this kind of transformation is the change of quartz into tridymite. On filling a crucible with pulverized quartz and heating it this change is manifested quite strikingly by the bursting of the vessel due to the increase in volume incident to this molecular change. This inversion



occurs at about 800°C. Similarly it is found that fused quartz which necessarily is in the amorphous condition is transformed to tridymite, which is shown by the dim-

ming of the glass. Since this change is reversible it follows that below  $800^{\circ}$  the tridymite reverts to quartz. This latter change is rather sluggish and requires considerable time, we can say, therefore, that quartz never crystallizes from mineral fusions excepting in the presence of catalyzers. Quartz\* then, is the unstable form of silica from  $800^{\circ}$  upward, and it will change to tridymite whenever opportunity offers. We have thus a volume change which on heating a clay is shown by the decrease in density. Purified natural quartz has a specific gravity of 2.654 ( $25^{\circ}$ ), while tridymite prepared from quartz has a density of 2.326; when prepared from fused quartz its density is 2.318. The density of quartz glass was found to be 2.213. On cooling a clay any change from tridymite to quartz stands for an increase in density, as must be evident from the above figures.

Similar inversions are known for meta and ortho calcium silicate. Thus we have the pseudo-hexagonal meta-silicate and wollastonite and three forms of the ortho calcium silicate. These are the alpha, beta and gamma modifications whose densities are 3.27, 4.28, and 2.97, respectively. There are doubtless other inversions which are not yet known to us.

Still another source of volume changes is to be sought in chemical reactions taking place in clay, such as the exothermic reaction taking place in clay substance at about  $1000^{\circ}$ , in which evidently an isomeric compound differing from the previous composition in structure is formed. Other examples are the change of calcium carbonate to the oxide, the interaction of lime and iron oxide, the formation of certain lime silicates above  $1200^{\circ}$ , the formation of spinels, magnetic oxide, etc. There must be many chemical reactions which at present are entirely unknown to us.

In studying the changes in the two specific gravities, then, we might be able to summarize the causes of the volume changes as follows:

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\*Day and Shepherd. Jour. Am. Chem. Soc., Vol. 28, p. 1099.

## A. Apparent specific gravity.

1. Inversion
2. Fusion
3. Chemical reactions
4. Pore space
5. Formation of "blebs"
6. Crystallization.

## B. True specific gravity.

1. Inversion
2. Fusion
3. Chemical reactions
4. Crystallization

A slight change common to both forms of specific gravity is that caused by the differences in the coefficient of expansion between the fused and crystalline portions. We observe, hence,, that the apparent specific gravity must be the algebraic sum of at least six and thee true specific gravity of four factors.

On heating a clay body the changes taking place in quartz and feldspar and perhaps in clay substance, the character of which has been discussed before, tend to increase the volume or to decrease the density. We might say, therefore, that, in terms of the density, the change is—in character. On cooling the clay, however, during the critical temperature intervals of each constituent inversed, the density change is+for then the inversion, as far as reversible, proceeds the other way. But since the cooling nearly always takes place far more rapidly than the heating up, it is quite probable that this change in volume is but slight.

We already know that the volume is increased on fusion and remains increased unless crystallization takes place on cooling. The change in density on fusion, hence, is—as far as most silicates are concerned.

Chemical reactions may cause either + or — changes, but on heating, according to the theorem of Le Chatelier, the changes are probably — in sign, as a rule.

The pore space, still remaining in the clay which has not yet been closed up by the softened or fused material of course, tends to decrease the apparent density. The same thing is true of the blebs formed by the evolution of

gases within the clay. This formation of gas is a very important factor in the mechanical strength developed in a clay, and this fact has been brought out very clearly by Purdy. In some clays the porosity thus contributed may be coincident with vitrification and hence, although the clay itself may be perfectly vitrified, the porosity curve would, in such a case, fail to indicate vitrification. Several such clays and bodies have been observed by the writers.

Crystallization would, in the nature of the case, take place only when the temperature has ceased to rise, that is, when the kiln is "soaking," the temperature just holding its own or when cooling begins.

That crystallization does take place to some extent in clays is established beyond a doubt. The senior writer in examining a section of paving brick which happened to show two well defined areas of properly burnt and over-burnt clay, found numerous crystals, needle-like in shape, in the over-burnt portion, but no evidence of crystallization in the sound part. Wegemann, in collaboration with Prof. Purdy, found considerable crystallization in over-burnt paving brick, fine needle-like crystals, yellowish-green in color, of unknown composition as well as minute crystals of iron oxide. Crystallization, as we know, stands for decrease in volume or increase in density, and hence we may say that it is a + change, in terms of the density.

The investigation which is the basis of this paper was carried on for the purpose of determining the character of the changes in the density and porosity of clay bodies to which various reagents have been added, burnt at different temperatures, and it is due Prof. Purdy to say that it was inspired by his paper on the pyrochemical and physical changes of clays. It was proposed to broaden the scope of the work and to determine, if possible, the following questions:

1. To what extent do the apparent specific gravity and porosity curves agree in indicating vitrification in the study of various additions to clays?

2. If there are any deviations where and how do they

occur, and what is their character? Are there any maximum or minimum points?

3. Under what conditions are certain substances fluxes, and when are they non-fluxes or refractories?

4. At what rate do these substances either accelerate or retard fusion?

5. At what temperatures does the fluxing or refractory character of certain additions begin?

6. What are the areas enclosed by some isothermals?

In the work of Purdy the specific gravity and porosity curves agree quite well in indicating vitrification, and hence it is but natural to inquire whether this is the case under all conditions. Any deviations might be reasonably ascribed to conditions pointing towards certain physical or chemical phenomena peculiar to the composition studied, since we know that the density changes with the transformation caused by chemical reactions, solution or crystallization.

The term flux is but a relative one, and no particular class of substances can be designated as fluxes. In a silicious material like clay, basic substances act as fluxes, while in basic compositions like Portland cement silicious compounds unquestionably behave as such. In addition we must consider the fact that a small portion of any substance, no matter what its composition, dissolved in another, will lower the fusing point, provided no chemical reaction takes place.

The rate of these changes is of interest in as much as this factor may have considerable influence upon the practical application. It may be either too rapid or too sluggish. In this manner we can establish the point at which no further change is observed and when additional amounts show no effect.

The question of temperature establishes the points at which the activity of the various additions become manifest and at what temperature the maximum effect is shown.

The areas enclosed by successive isothermal curves are designed to show the rate at which vitrification progresses,

and the composition of the fusible combination as well as the change in the composition on raising the temperature. It might be said that thus the changes in the eutectic combinations are indicated.

The clays upon which the effect of various substances was studied were as follows:

1. Florida kaolin, and in several instances, Georgia kaolin.
2. Ball clay, Tennessee No. 3.
3. Shale from Galesburg, Ill.
4. Shale from Crawfordsville, Ind.
5. Shale from Canton, Ohio.

The materials added to the above clays were as follows:

- |                   |                         |
|-------------------|-------------------------|
| 1. Feldspar       | 6. Feldspar-flint       |
| 2. Whiting        | 7. Whiting-flint        |
| 3. Ferric oxide   | 8. Ferric oxide-flint   |
| 4. Flint          | 9. Ferric oxide-whiting |
| 5. Florida kaolin | 10. Cornish stone       |

The composition of some of the materials are given in the following table:

	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	FeO %	TiO <sub>2</sub> %	CaO %	MgO %	K <sub>2</sub> O %	Na <sub>2</sub> O %	Loss on ig- nition. %	Mois- ture %
Galesburg* Shale .....	63.62	16.31	6.22	2.88	0.96	0.63	1.44	2.60	1.50	6.26	0.38
Crawfordsville* Shale .....	68.50	16.98	5.77	.....	.....	0.99	1.71	2.97	.....	7.33	0.27
Canton* Shale .....	55.51	22.21	7.26	.....	.....	0.56	1.63	3.56	.....	8.00	.....
Feldspar .....	68.22	17.83	.....	.....	.....	0.30	0.11	12.13	1.90	0.35	.....
Flint .....	98.00	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Iron Oxide.....	.....	.....	99.00	.....	.....	.....	.....	.....	.....	.....	.....
Whiting .....	1.62	3.50	.....	.....	.....	52.65	.....	.....	.....	.....	0.50

\*Purdy and Moore, Trans. Am. Cer. Soc., Vol. 9.

The compositions are expressed in percentages throughout, since the changes to be noted are shown in this manner as well as if molecular relations had been employed. In fact, considering the heterogeneous character of the clays used and their physical differences, the consideration of chemical formula would have appeared to be almost absurd. This is especially true since we were dealing only with the vitrification and not the fusion of bodies, and particularly since the earlier stages of vitrification were of special interest to us.

The materials were weighed out in the dry condition, and usually the two ends of a series were ground dry in the ball mill for two hours. From the two end compositions the intermediate mixtures were obtained by blending and thorough grinding in a mortar. Each batch was then made up with water to the desired consistency, and after thorough wedging was molded into a brickette of the dimensions: 12.8x7.8x1.3 cm. in a brass mold provided with a movable bottom. Each brickette was cut up into eight prisms, which were stamped with the series numbers. After thorough drying one brickette from each mixture was taken and placed in a sagger. Each burn, therefore, contained one of the eight small brickettes of every composition. The saggars were placed and cones put in the kiln, well protected from any direct flame. The kiln used was a down-draft test kiln, fired with coke, and has been described in the paper on "Fritted Glazes" by R. C. Purdy and H. B. Fox.\* The firing temperatures were cones 09, 06, 03, 01, 2, 4, 6; some brickettes which had been left by Prof. Purdy as part of an unfinished investigation were fired to cones 9, 11, and 13. The cooling of the kiln was hastened in no case, though the damper was left open.

The brickettes when cold were freed from adhering particles, weighed, and immersed in distilled water for 48 hours; they were then boiled for one hour and finally placed in a large suction flask connected to a filter pump

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\*Trans. Am. Cer. Soc., Vol. IX.



and left there until no more air bubbles were given off, which usually took several hours. This method was found to be more satisfactory than exhaustion by an air pump, as it seemed to result in better absorption of water. The brickettes were then suspended in water by attaching with a silk thread to the beam of the balance and thus weighed. Immediately afterwards they were weighed in air, thus giving the wet weight. The specific gravity was calculated by the usual formula and the porosity by the Purdy formula.

Several hundred pycnometer specific gravity determinations were also made on the dried and pulverized brickettes by weighing a quantity of the powder in the pycnometer and filling the pycnometer a little more than half full of warm water. The pycnometer was then attached to a bent 50 cc. pipette, which contained some water. The other end of the pipette was connected to the filter pump and the air exhausted from the powder. The vacuum was sufficient to cause the water in the pycnometer to boil at a temperature of about  $30^{\circ}$ . After no more air bubbles were evolved the pycnometer was filled by raising the pipette and allowing the air-free water to run into the apparatus. In making these determinations special pains were taken to dry the powder in an air bath at a temperature never less than  $120^{\circ}$ . Some of the pycnometers were collapsed by the air pressure.

Comparing the specific gravities by the two methods the differences are shown to be of the following order of magnitude:

Spec. gr. pycnom. ....	2.69	2.62	2.73	2.76	2.65	2.66	2.67	....	....
Spec. gr. suspension ....	2.55	2.51	2.54	2.56	2.57	2.58	2.61	....	....
Difference .....	0.14	0.11	0.19	0.20	0.08	0.08	0.06	....	....
Spec. gr. pycnom. ....	2.68	2.65	2.65	2.64	2.64	2.67	2.67	....	....
Spec. gr. suspension ....	2.62	2.61	2.59	2.61	2.57	2.63	2.59	....	....
Difference .....	0.06	0.04	0.06	0.03	0.07	0.04	0.08	....	....
Spec. gr. pycnom. ....	2.66	2.65	2.67	2.64	2.64	2.64	2.67	....	....
Spec. gr. suspension ....	5.56	2.61	2.61	2.62	2.61	2.58	2.59	....	....
Difference .....	0.10	0.04	0.06	0.02	0.03	0.06	0.08	....	....
Spec. gr. pycnom. ....	2.65	2.67	2.66	2.70	2.67	2.70	2.67	2.68	....
Spec. gr. suspension ....	2.60	2.61	2.60	2.59	2.60	2.68	2.66	2.64	....
Difference .....	0.05	0.06	0.06	0.11	0.07	0.02	0.01	0.04	....
Spec. gr. pycnom. ....	2.70	2.65	2.67	2.70	2.71	2.78	2.73	2.72	2.59
Spec. gr. suspension ....	2.62	2.62	2.61	2.66	2.60	2.80	2.58	2.69	2.51
Difference .....	0.08	0.03	0.06	0.04	0.11	0.07	0.15	0.03	0.08

The sensibility of weighing in the pycnometer experiments was about 0.5 milligram for one balance and 1 milligram for another, the average sample of powdered material averaging 8 grams. The error of weighing thus varies from 0.005 to 0.01 per cent. In the suspension method the weight of the brickettes varied from 15 to 20 grams. The sensibility of the balances was about 2 centigrams, which corresponds for the 15 gram brickette to a variation of 0.13 per cent.

From these results it is clearly seen that the specific gravity determinations by suspension are greatly affected by the porous structure of the clay, that is, by the pores into which water cannot penetrate. It was recognized that in order to obtain comparable specific gravity curves the true specific gravity would have to be used. But since these determinations consume much more time, and the main aim of the experiments planned was chiefly a practical one, it was decided to use only the apparent specific gravities and porosities in obtaining the rates of vitrification, since after all it is the *rate* and not the absolute values that interested the writers most at the time. The study of the true specific gravities has been reserved

for mixtures whose components have themselves been defined more closely by chemical and physical methods, and which are intended to be simple mixtures rather than such complex ones as are afforded by the shales. By this method it was possible to cover the ground more rapidly, and about 4000 determinations were made. Owing to this large mass of data it is impossible to reproduce all of the rate curves thus obtained, and hence only the typical cases are presented.

We shall now discuss the additions of the various reagents to the clays mentioned above.

#### FELDSPAR.

Feldspars are considered neutral body fluxes. By this is meant that their fluxing effect is additive, they being simply solvents of the clay substance and the free silica. Feldspar naturally lowers the melting point of a body most when it is added to the eutectic combination of kaolin and quartz, which corresponds to the ratio of 1:3. This is shown very clearly in the clever work of Dr. M. Simonis\* on "The Fusion Points of Mixtures of Zettlitz Kaolin, Quartz and Feldspar Expressed in Cones."

By means of a simple arithmetical expression, for which he claims no theoretical or scientific significance, though he suggests its practical use, he calculates the refractory quotient for bodies high in clay and high in quartz. In the first case, that is, in clayey bodies in which the per cent of kaolin is greater than one-third of the per cent of quartz, or where  $K > \frac{qu}{3}$  Simonis obtains his refractory quotient by the formula

$$R. F. = K - \frac{qu}{3} - f + 60,$$

where  $K = \% \text{ kaolin}$

$qu = \% \text{ quartz}$

$f = \% \text{ feldspar.}$

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\*Sprechsaal, Vol. 40, Nos. 29 and 30.

For silicious bodies in which

$$K < \frac{qu}{3}$$

the formula employe is:

$$R. F. = \frac{\frac{qu}{3} - K}{2} - f + 60.$$

The number 60 is added to prevent negative values. The values of the refractory quotient are translated into cone temperatures by the following table:

Refractory quotient .....	17.5	22.6	28.0	33.7	39.2	44.6	50.0	57.6
Melting point in cones.....	14.0	15.0	16.0	17.0	18.0	19.0	20.0	26.0
Refractory quotient .....	65.0	72.0	80.0	89.0	102.0	114.0	127.0	141.0
Melting point in cones.....	27.0	28.0	29.0	30.0	31.0	32.0	33.0	34.0

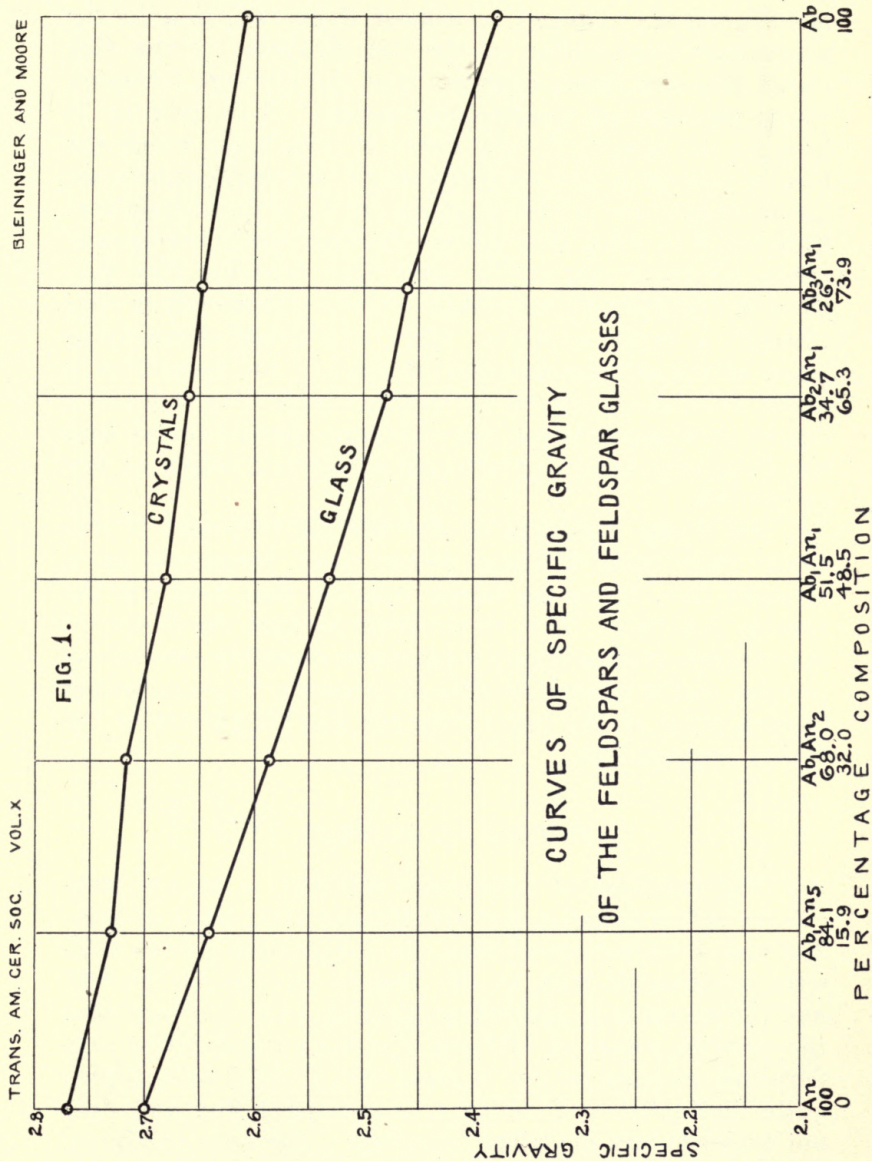
From the consideration of the Simonis calculation it is evident that feldspar plays the role of a neutral flux.

With regard to the fusion process of triclinic feldspars we have accurate data referring to artificial spars,\* which had the following composition:

	An	Ab <sub>1</sub> An <sub>5</sub>	Ab <sub>1</sub> An <sub>2</sub>	Ab <sub>2</sub> An <sub>1</sub>
SiO <sub>2</sub> .....	43.33	47.10	51.06	60.01
Al <sub>2</sub> O <sub>3</sub> .....	36.21	34.23	31.50	24.95
Fe <sub>2</sub> O <sub>3</sub> .....	0.29	0.15	0.22	0.29
CaO .....	20.06	17.00	13.65	7.09
Na <sub>2</sub> O .....	0.11	1.74	3.68	7.79

We have here evidently mixtures of albite and anorthite, and on fusing a series of these mixtures it was found that they proved to be a series of solid solutions whose

\*Day and Allen. The Isomorphism and Thermal Properties of the Feldspars, Carnegie Inst., 1905.



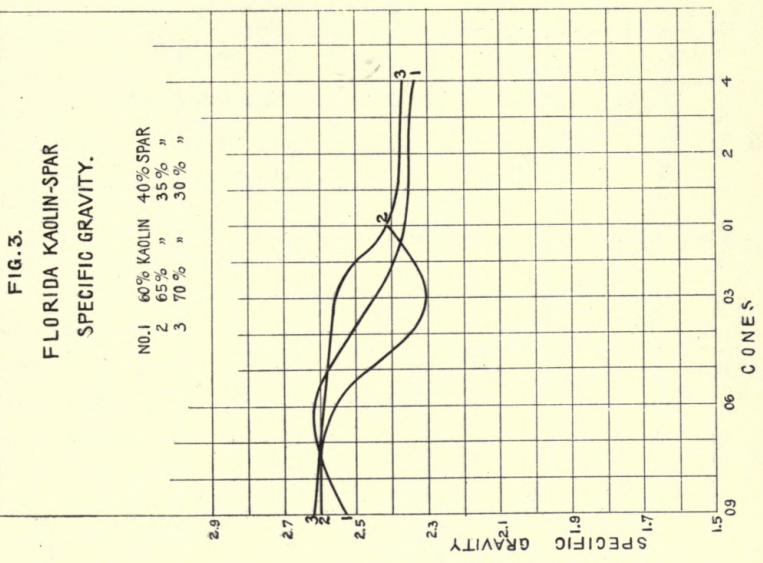
melting points changed in almost linear relation to the percentage composition of the two silicates. From this result Day and Allen conclude that the triclinic feldspars "form together an isomorphous series." This relation is brought out clearly by the curve of Fig. 1, in which the rate of change in the specific gravity of mixtures between the anorthite and albite is shown to be a linear relation. This tends to show that we are dealing here with isomorphous mixtures and at the same time explains why they have no definite melting points. Albite was proven to melt through a range of about  $150^{\circ}$ . Although the melting point of the average feldspar as used in the industries is about at cone 8, yet its interaction with clay substance begins at a much lower temperature. Berdel found that the dissolving action of orthoclase feldspar began as low as cone 09.

On fusing mixtures of the trilinear feldspars it was found that their melting points were connected by a straight line, the same linear relation that held for the specific gravities. This shows likewise that the fusion of the triclinic feldspars is a continuous smoothly proceeding process, and it is even possible to calculate the composition of each point on the curve from the specific gravity or the fusion temperature.

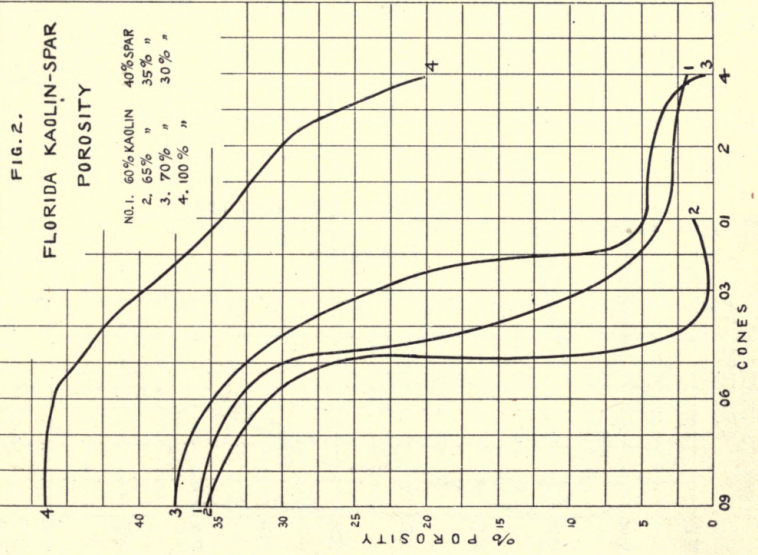
#### ADDITION OF FELDSPAR.

The behavior of orthoclase feldspar is shown sufficiently in the porosity and specific gravity curves of Figs. 2, 3 and 4. We observe that the vitrification due to feldspar is indicated both by the drop in the specific gravity and the decrease in porosity. We also find confirmed that the solution effect of feldspar begins at quite a low temperature, at least as low as cone 06. It is likewise shown quite distinctly that feldspar is a neutral flux and does not undergo any chemical reactions. The only minimum is that due to the eutectic mixture which, however, was not fixed in these series. The solution of kaolin by feldspar

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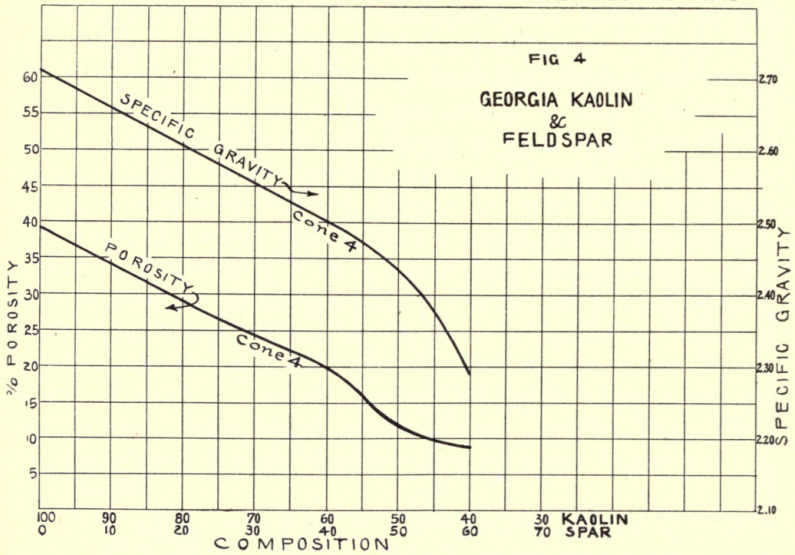


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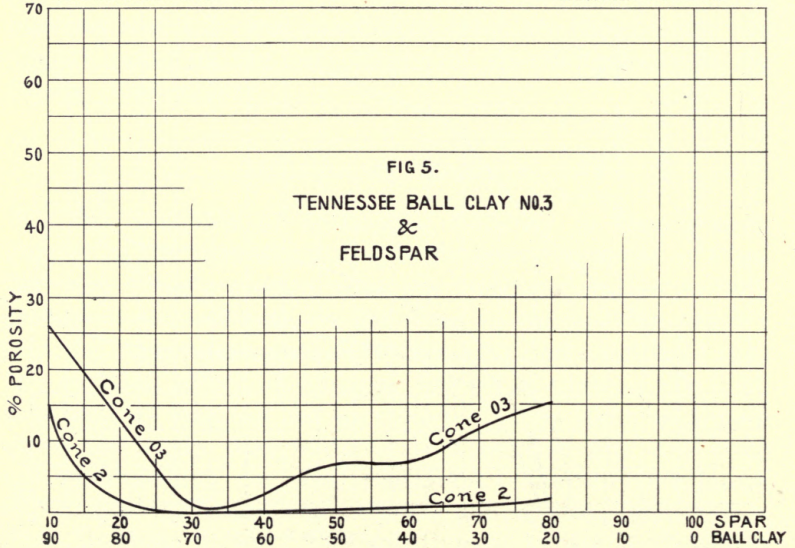




FIG. 6  
CANTON SHALE-SPAR  
POROSITY.

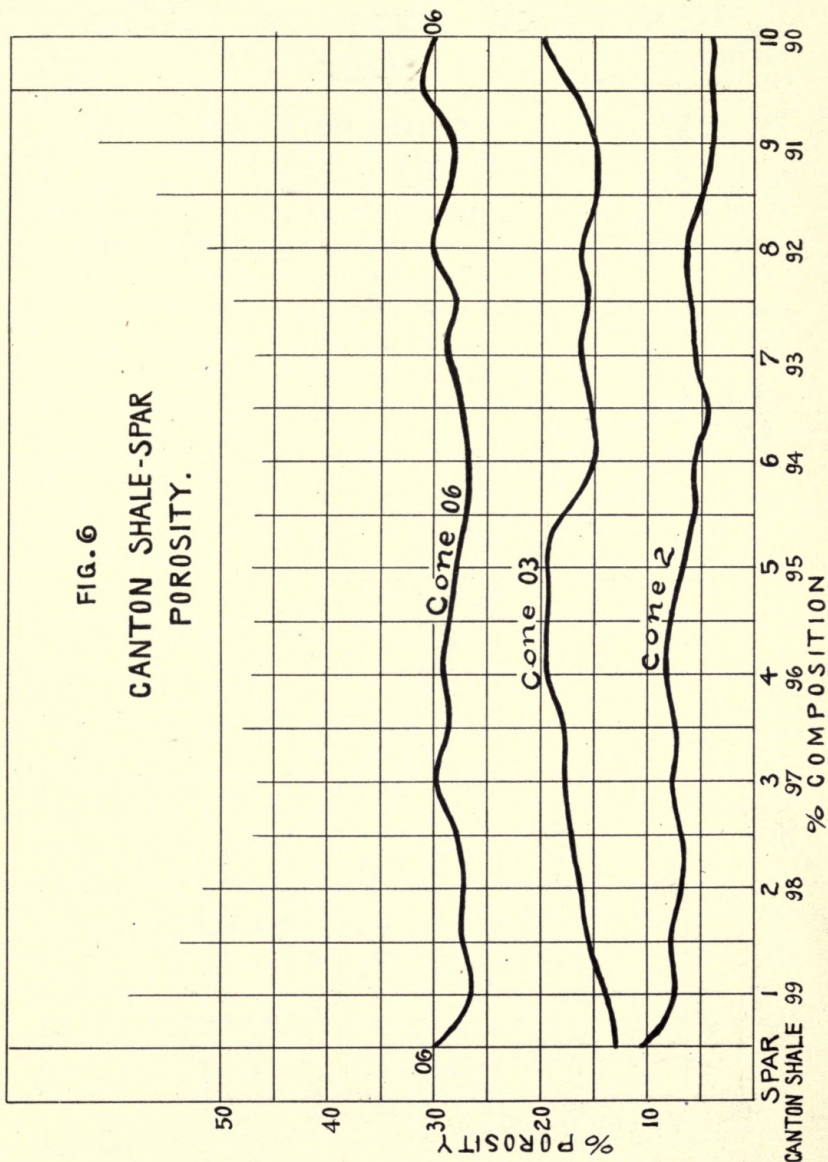
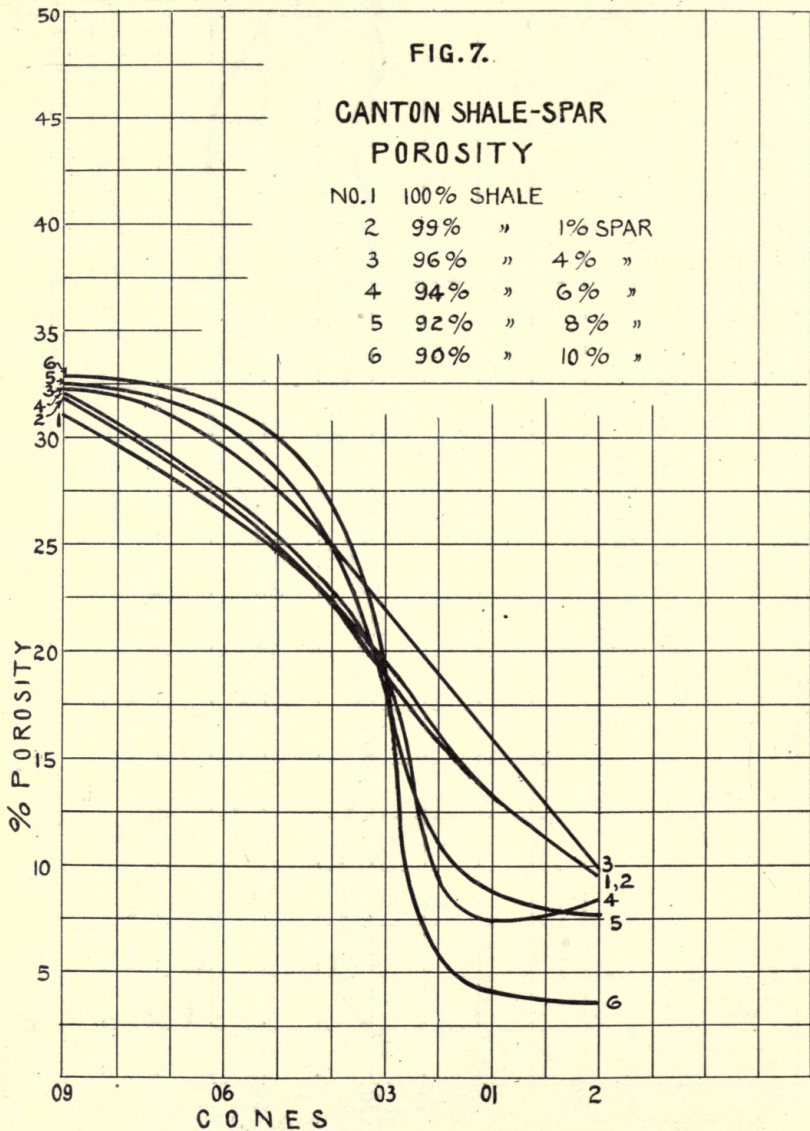


FIG. 7.

CANTON SHALE-SPAR  
POROSITY

NO. 1	100% SHALE	
2	99% "	1% SPAR
3	96% "	4% "
4	94% "	6% "
5	92% "	8% "
6	90% "	10% "



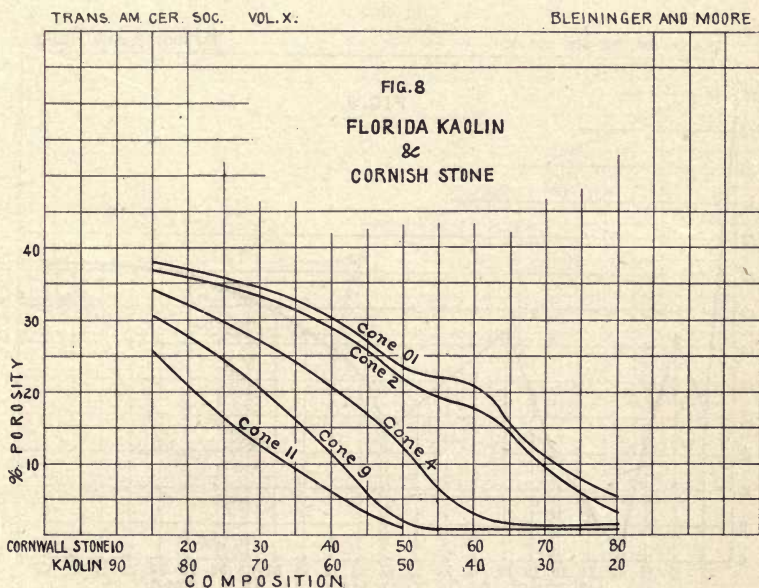
takes place at a fairly rapid rate, which shows simply that there seems to be no physical obstacle to this mutual solution.

The curves also bring out the difference in the behavior of Georgia kaolin and Florida kaolin.

In Fig. 5 we have the porosity curve of mixtures of Tennessee ball clay No. 3 with feldspar, and it is evident that feldspar in this case becomes far more potent in its action than in the cases of the two kaolins.

The effect of various percentages of feldspar upon Canton shale is shown in Fig. 6, and we observe that though the first additions cause a small decrease in porosity, the result shows practically no gain in fusibility or vitrification. The same fact is brought in Fig. 7, in which some of the shale-spar curves are arranged.

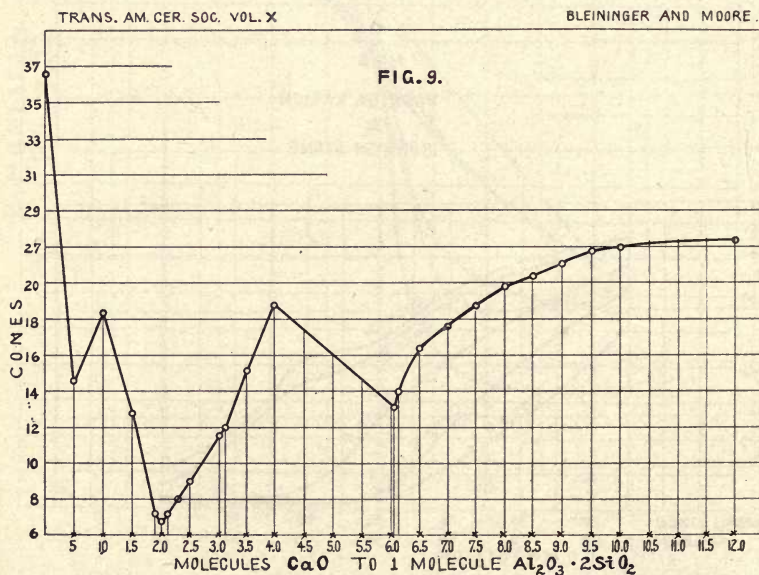
In this connection it was also interesting to observe the action of Cornish stone on kaolin as shown by Fig. 8.



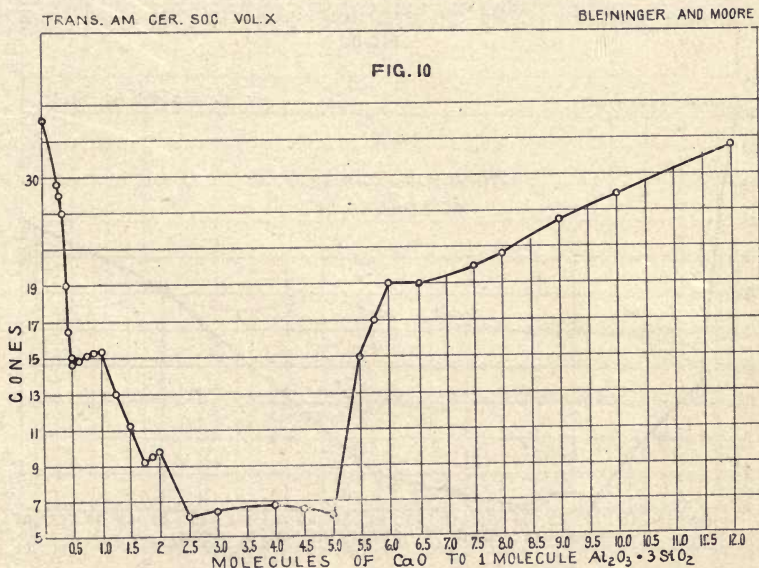
Here we note distinctly the slow, neutral fluxing effect of this material whose action is more gradual than that of the feldspar and which offers the safest flux, as far as range and rate of vitrification are concerned.

#### THE ADDITION OF LIME.

*Kaolin and Ball Clay.* In the addition of calcium carbonate to clays we are dealing with a flux which is unlike feldspar or Cornish stone. Its action is not gradual, but variable; that is, though its presence may not be observed by means of the porosity curve, at the proper reaction temperature it suddenly combines and causes as large an amount of fusible magma to be formed as is consistent with the composition of the body. At the same time there is to be considered the fact that lime-alumina-silica compounds form a number of maximum and minimum fusing compounds. This has been clearly shown in the work



of Rieke,\* who investigated the melting points of mixtures of this kind in a most thorough and exhaustive piece of work, using an electric carbon resistance furnace for the determination of the melting points. We shall consider only his results, referring to the  $Al_2O_3 : 2 SiO_2$  mixtures and those higher in silica. The first curve brings out the fact already noted by Cramer† that for high temperatures, additions of CaO to kaolin, up to 10%, decrease the melting point in equal intervals. The lime-kaolin fusion curve of Rieke is reproduced in Fig. 9, the abscissa indicating the molecules of CaO to 1 molecule of  $Al_2O_3 : 2 SiO_2$ , the ordinates the melting points in cones. With a content of 10% CaO we have a minimum corresponding to the formula  $CaO, .2 Al_2O_3, .4 SiO_2$ . On increasing the lime we find a maximum at the composition  $CaO : Al_2O_3 : 2 SiO_2$ . With more lime the fusion curve descends again to a mini-



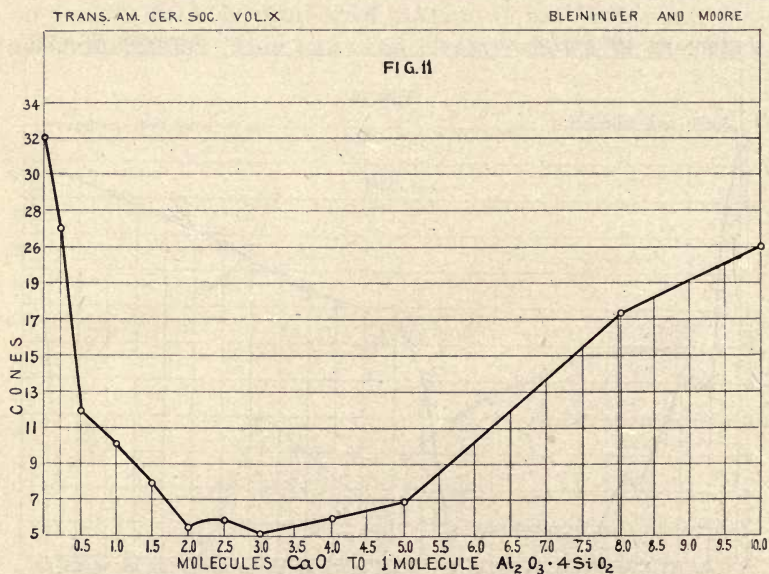
\*Sprechaal, Vol. 40, Nos. 44, 45, 46.

†Tonindustrie-Zeitung, 1887, p. 197, and 1888, p. 73.

imum  $2 \text{ CaO} : \text{Al}_2\text{O}_3 : 2 \text{ SiO}_2$ , which is the most fusible combination between kaolin and lime that exists corresponding to a percentage composition of 36.1%  $\text{SiO}_2$ , 30.5%  $\text{Al}_2\text{O}_3$  and 33.4%  $\text{CaO}$ . On increasing the lime still more Rieke obtained a second maximum at  $4 \text{ CaO} : \text{Al}_2\text{O}_3 : 2 \text{ SiO}_2$ .

This is followed by a third minimum  $6 \text{ CaO} : \text{Al}_2\text{O}_3 : 2 \text{ SiO}_2$ . After this it appears that no further decrease in melting point occurs. Since the maximum and minimum points very likely correspond to chemical combinations, it seems, according to Rieke, that there exist at least four distinct compounds of lime and kaolin.†

In the mixtures of  $\text{CaO}$  with  $\text{Al}_2\text{O}_3 : 3 \text{ SiO}_2$  shown in Fig. 10, there are observed four maxima and four minima which appear to show the existence of the following compounds and mixtures:



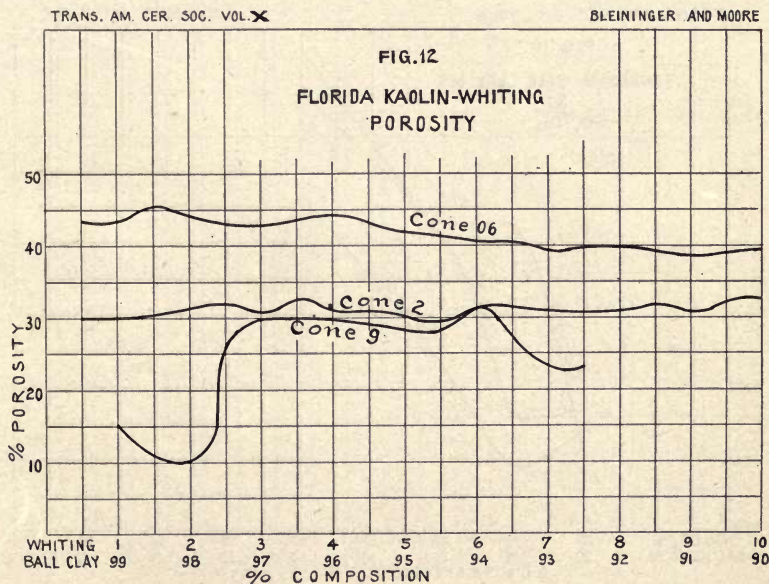
†Rieke's view that the minimum as well as the maximum points correspond to chemical compounds is open to criticism. The minimum points are probably eutectic mixtures.

CaO	2	Al <sub>2</sub> O <sub>3</sub>	6	SiO <sub>2</sub>	6	CaO	Al <sub>2</sub> O <sub>3</sub>	3	SiO <sub>2</sub>	
7	CaO	4	Al <sub>2</sub> O <sub>3</sub>	12	SiO <sub>2</sub>	2	CaO	Al <sub>2</sub> O <sub>3</sub>	3	SiO <sub>2</sub>
3	CaO	Al <sub>2</sub> O <sub>3</sub>	3	SiO <sub>2</sub>	3	4	CaO	Al <sub>2</sub> O <sub>3</sub>	3	SiO <sub>2</sub>
5	CaO	Al <sub>2</sub> O <sub>3</sub>	3	SiO <sub>2</sub>	3	6	CaO	Al <sub>2</sub> O <sub>3</sub>	3	SiO <sub>2</sub>
13	CaO	2	Al <sub>2</sub> O <sub>3</sub>	6	SiO <sub>2</sub>					

Finally in mixtures of lime with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> Rieke found one rather indistinct maximum, 5 CaO : 2 Al<sub>2</sub>O<sub>3</sub> : 8 SiO<sub>2</sub> and two minima, Fig. 11. The curve as a whole is more regular than the preceding ones.

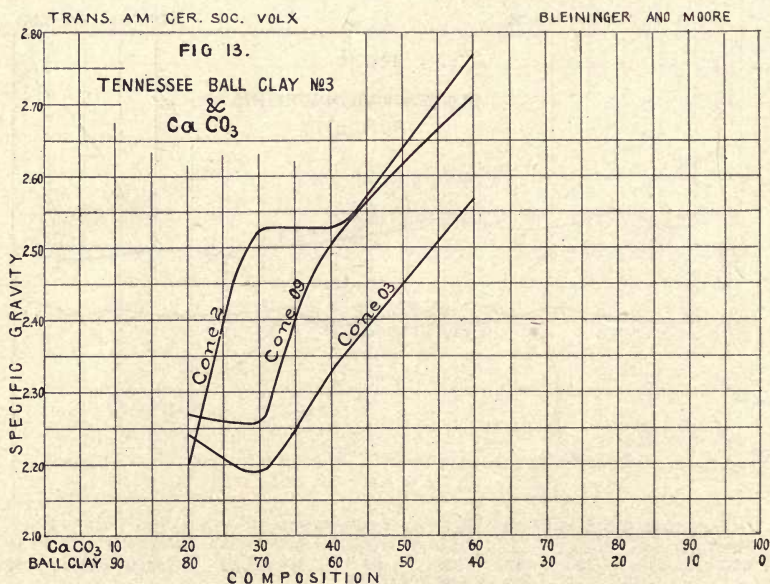
It is evident from these data that we cannot expect from lime-clay mixture the regularity of fusion induced by feldspathic fluxes, and it remains to be seen how the vitrification of different clays is affected by this flux.

*Lime—Florida Kaolin Mixtures.* Inspection of curve of Fig. 12 shows clearly that with increasing lime content at Cone 06 but little change occurs within the compositions examined, the mixture containing 10% whiting showing



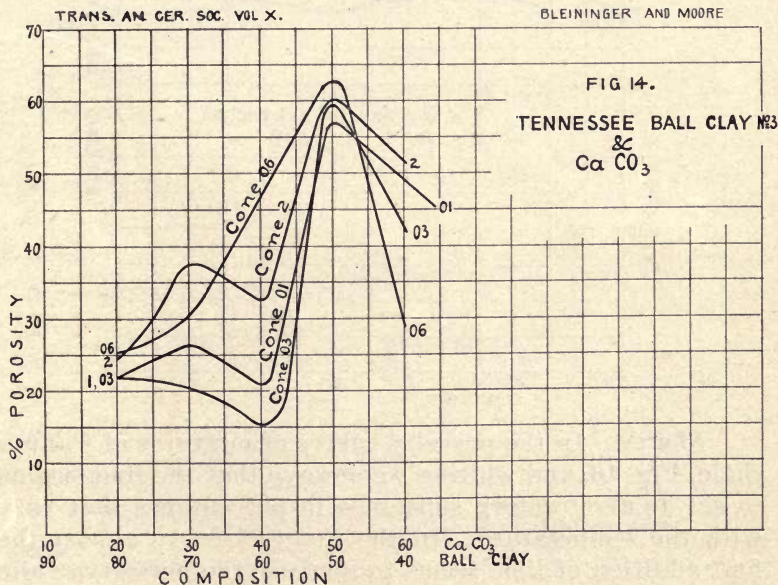
only 4% less porosity than the composition 99.5% kaolin, 0.5% whitening. We also observe that the first 2% of whitening in the Cone 9 curve are more effective in decreasing porosity than 3-6%, a second decrease in porosity taking place only beyond 6% whitening. Of course this is in agreement with the general theory of dilute solutions as suggested by Ludwig.

On studying mixtures of ball clay and larger amounts of lime we observe in the specific gravity curve, Fig. 13, a distinct minimum in the Cone 09, 03, and 2 burns at about 30% whitening and 70% ball clay, which corresponds roughly to the minimum  $\text{CaO}:\text{Al}_2\text{O}_3:2\text{SiO}_2$  observed by Rieke. This seems to be the eutectic composition under these temperature conditions. The corresponding porosity curve, Fig. 14, shows two maxima and minima, the first maximum being at 30% whitening and 70% ball clay, the second at 50% clay, 50% whitening. The minimum is at 40% whitening, 60% ball clay, a second minimum is indicated, but not

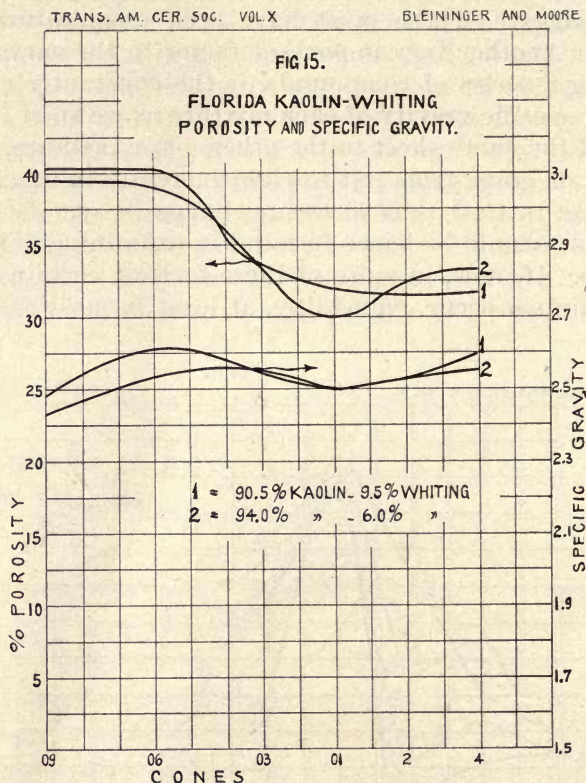




reached. Of course it would be idle to claim that these maximum points actually do represent certain compounds, as we must remember that the apparent specific gravities are the resultants of a number of factors, of which not the least important is the temperature to which each brickette was raised in the kiln. It would be claiming too much to say that each brickette actually reached or did not exceed the temperature of the burn as indicated by the cone in each sagger. There must have been temperature differences. Another very important factor in the curves representing a series of compounds, is the constantly changing initial specific gravity of each mixture as we start from one side of the curve sheet to the other. For instance, the last series, on going from left to right increases in lime. Every increase in CaO thus means a change in specific gravity, and this should be borne in mind in examining subsequent curves. If, now, in spite of these factors, certain maxima and minima occur, coinciding, at least in most cases, with



similar points in the porosity curves, we are led to the conclusion that certain phenomena are taking place. The technical side of the vitrification progress is represented, of course, by the porosity curves. In Fig. 15 the action of 6 and 9.5% respectively of whiting is shown for the lower temperatures, and we observe that the decrease in porosity begins about between cones 06 and 01.

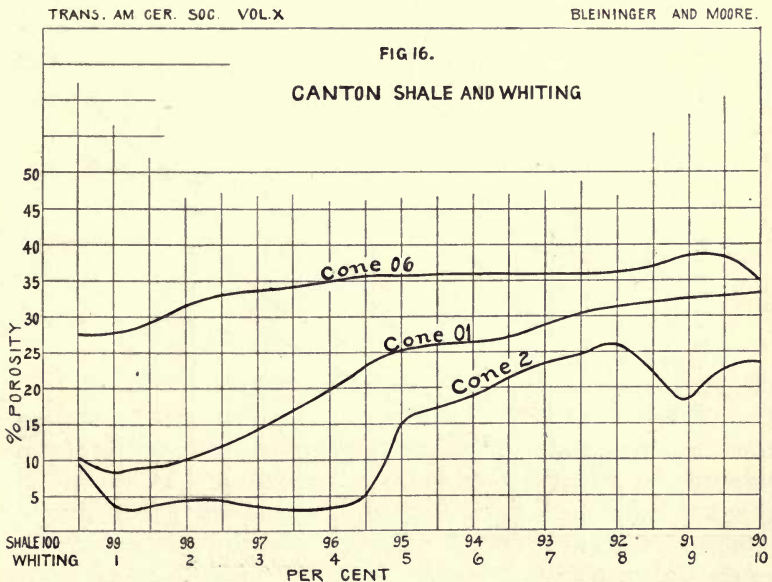


*Shales.* In the porosity curves of mixtures of Canton shale, Fig. 16, and whiting we observe that the lime begins to act as a refractory substance in percentages that vary with the temperature. In the Cone 06 curve almost the first addition of lime seems to increase the porosity, while

the increase in the Cone 01 and 2 curves begins with 1.5 and 4.5% respectively. The significance of the minimum with the 9% addition, if it really is a minimum, remains to be explained. From general considerations it appears that the porosity at about that point ought to decrease.

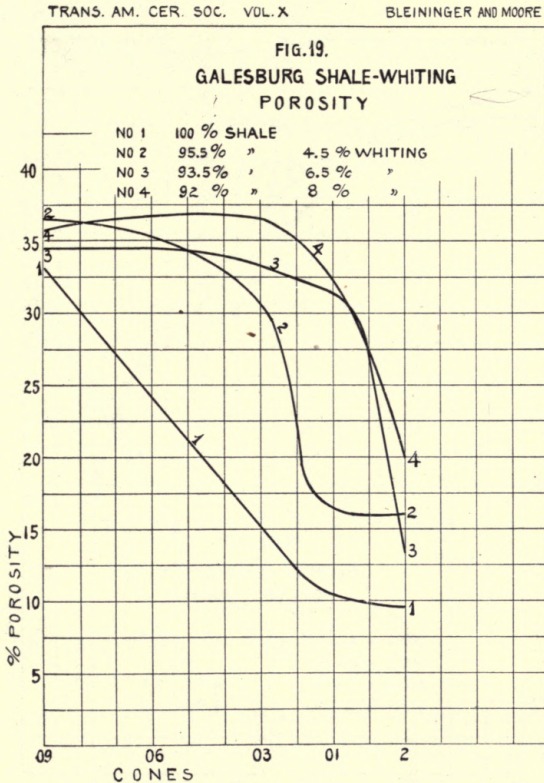
The rate at which this shale decreases in specific gravity and porosity is shown in Fig. 17, and brings out the fact that the porosity tends to increase up to Cone 06, and from this point on shows a rate of decrease slower than that of the pure shale. But after passing Cone 03 its vitrification becomes decidedly more rapid than that of unmixed shale, as we know to be the effect of lime.

In Fig. 18, representing mixtures of Crawfordsville shale and whiting, we observe a very decided increase in porosity between Cones 06 and 03, followed by an extremely sudden drop between 03 and 01. The increase in porosity after vitrification has been reached is also quite marked in some of the lower lime mixtures.



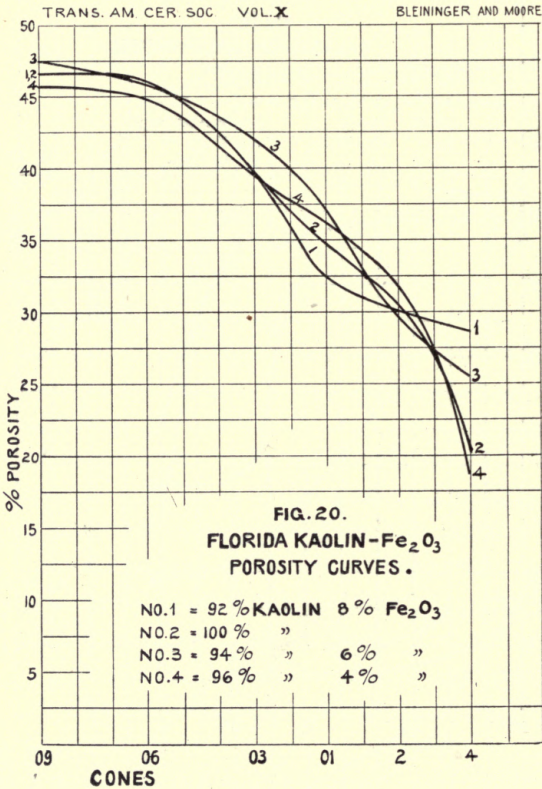


The Galesburg shale, Fig. 19, was less affected by the lime added than the two other shales at Cone 2, but at Cone 4 the mixtures had gone considerably beyond viscous vitrification and had stuck to the saggars.



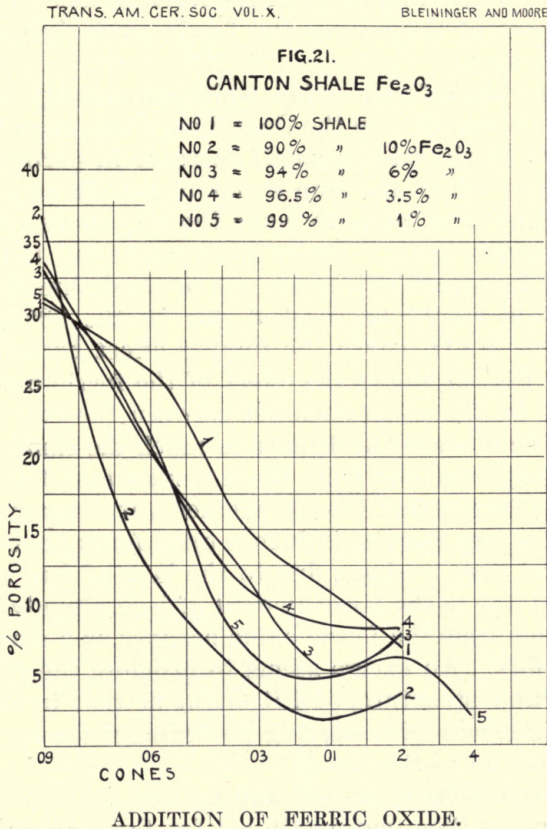
With regard to the effect of lime introduced as the carbonate we may say, therefore, that it is not a neutral, gradual flux, but evidently there are produced several combinations of lime with the other constituents of the clay which are available, which give rise to curves showing maximum and minimum points. This is the case especially with larger amounts of lime. This effect naturally is more

prominent at higher temperatures. The fluxing effect of small amounts of lime on high alumina clays is not marked at lower temperatures, as evidently such temperature as Cone 2 are not yet within the temperature zone of its activity.



In ferruginous shales containing lime the maximum fluxing effect is shown by not more than 5% of the carbonate. Any increase above this amount seems to produce refractoriness at temperatures up to Cone 2 inclusive. The amount of lime drawn into reaction increases with the temperature; while at Cone 06 it does not seem to have

taken part in the condensation of the body, at Cone 01 its effect is noticeable. In regard to its general behavior in a paving brick shale we must say, of course, that it is an undesirable constituent, not only because of its sudden fluxing effect, but also because of its tendency to produce vesicular structure.



In the series in which we have mixtures of clay with increasing amounts of ferric oxide, it is evident that each increase in iron results in an increase of specific gravity, and hence specific gravity curves are of little value in this connection.

*Florida Kaolin.* From Fig. 20 we observe at once that iron oxide is by no means an active flux when combined with clay substance, for while a small amount seems to exert some fluxing action, its general tendency seems to be a rather indifferent behavior. The areas inclosed by the 100% kaolin and the kaolin-iron mixture curves give some measure of the fluxing effect of the ferric oxide. It is noted that in part of the curves the ferric oxide behaves as a refractory agent.

In the shale-ferric oxide series practically the same effects are observed. In the Cone 2 curve up to an addition of 2.5% of ferric oxide a small decrease in porosity is observed, after which the iron seems to behave as a neutral agent. More iron tends to make the clay more refractory up to a certain point. There is no doubt but that, if the iron were increased still more, one or minimum and maximum points would be reached, for in the 90% Canton shale—10%  $\text{Fe}_2\text{O}_3$  curve the fluxing effect becomes quite marked. Fig. 21 shows the effect of the ferric oxide upon this shale by the areas enclosed between the two porosity curves. The other shales behave in much the same manner.

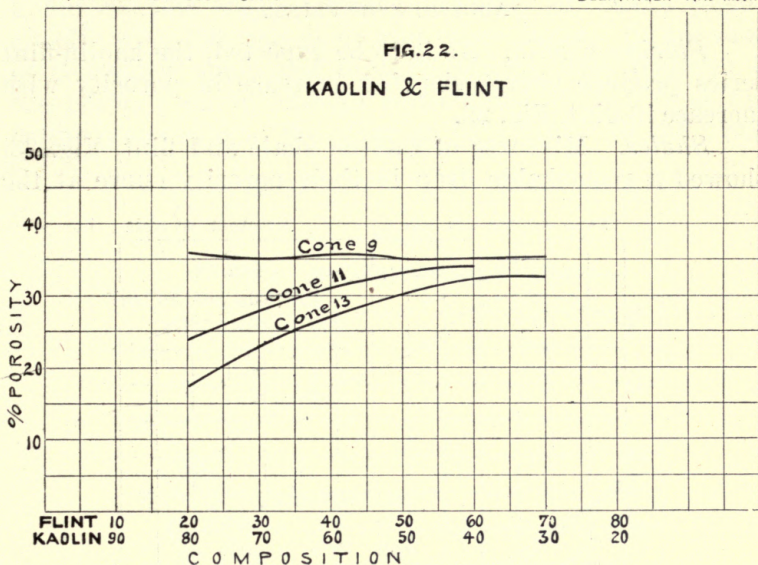
We may conclude from these results that ferric oxide is not an effective flux when combined with clay substance, nor has it a very marked influence upon ferruginous shales. In the first case, perhaps due to the lack of free silica, in the second due to the large amount of iron already present. At the same time the ferric oxide behaves as a slow acting and safe flux. An excess seems to promote the formation of a vesicular structure, and it might be that in the shale-iron oxide curves with varying percentages the increase in porosity is due to this cause.

The hypothetical case of adding iron oxide to clays in order to make them more suitable for the manufacture of paving brick seems, therefore, not to be well taken, though some patent specifications prescribe such a mixture.



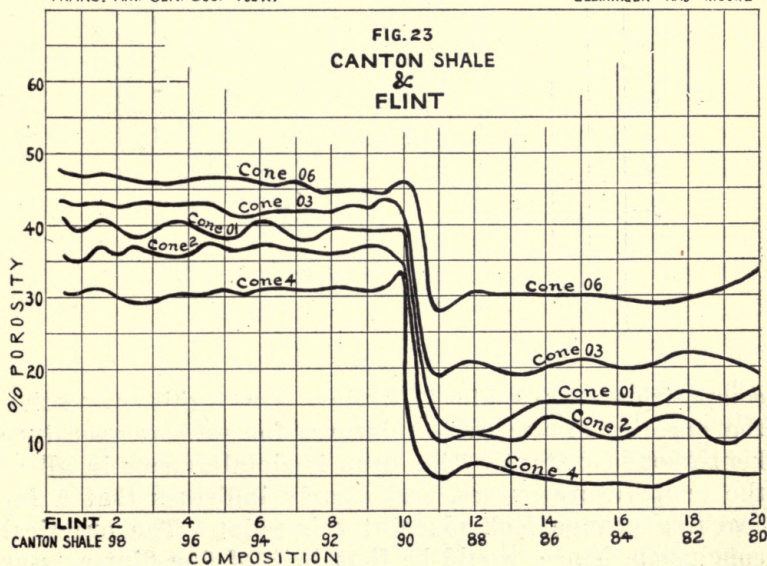
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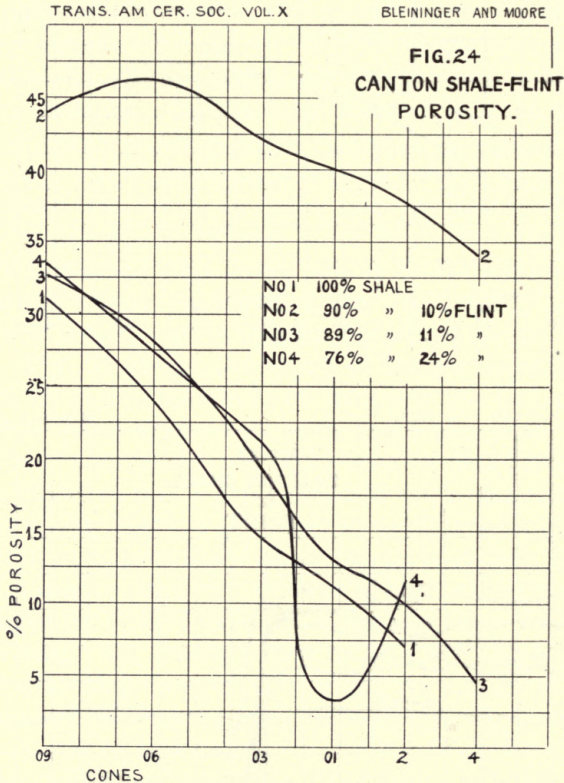
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ADDITION OF FLINT.

*Florida Kaolin.* As is to be expected, the kaolin-flint series produce curves showing increase in porosity with increase in flint, Fig. 22.

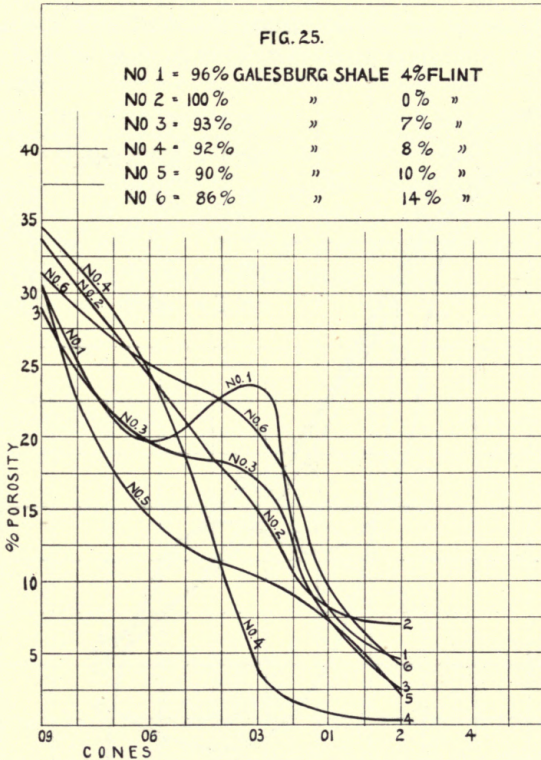
*Shales.* Mixtures of Canton shale and flint, Fig. 23, showed a remarkable drop in their porosity curve at the



composition, 90% shale, 11% flint. Up to this proportion the porosity of the shale mixtures for each temperature kept about constant. This drop is simultaneous in all of the temperature curves, and clearly indicates that a far reaching change took place at this point. The practical conclusion, hence, would be that 10% of fine flint acts as

a flux in this shale, forming probably an easily fusible silicate with the iron oxide and other fluxes. In mixtures of Galesburg shale and flint two drops were observed in the porosity curve, though neither one of them was well defined, one at 8%, the other at 18% flint. In the Craw-

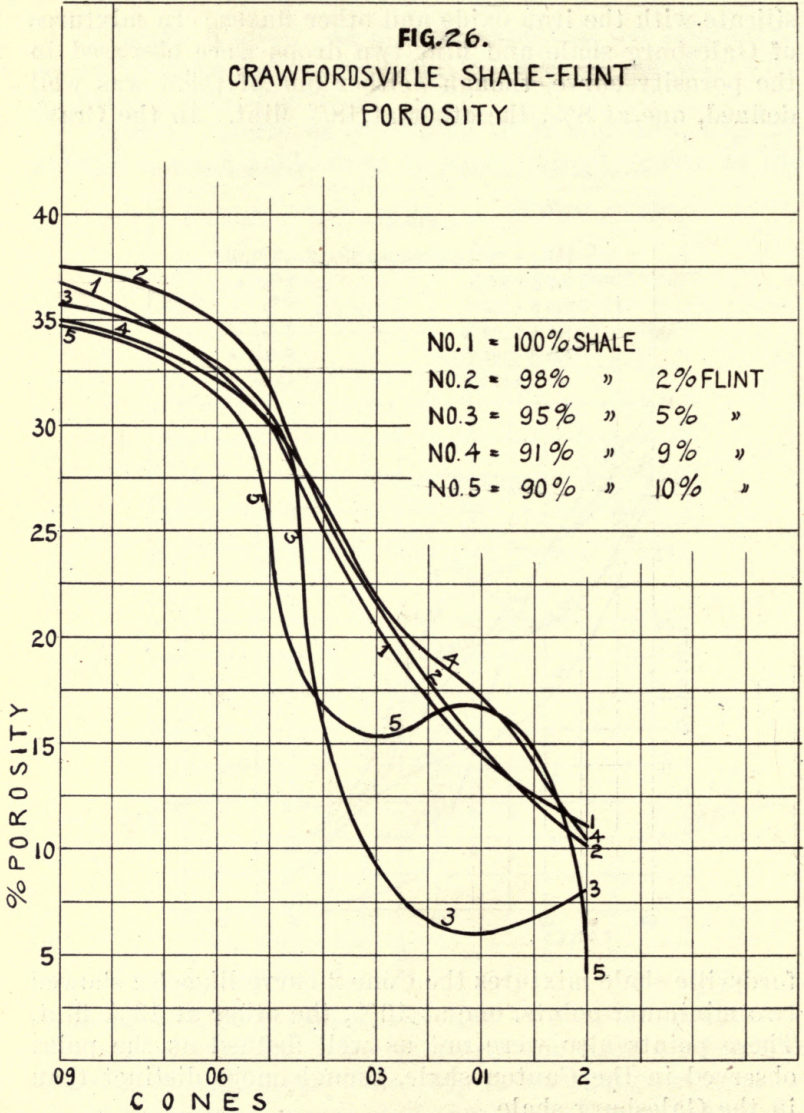
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fordsville shale mixtures the Cone 2 curve likewise showed two minimum points, one at 10%, the other at 19% flint. These points also were not as well defined as the point observed in the Canton shale, though more distinct than in the Galesburg shale.

Referring to the absolute fluxing effect, there is no gain as regards increase in fusibility by the addition of

**FIG. 26.**  
**CRAWFORDSVILLE SHALE-FLINT**  
**POROSITY**



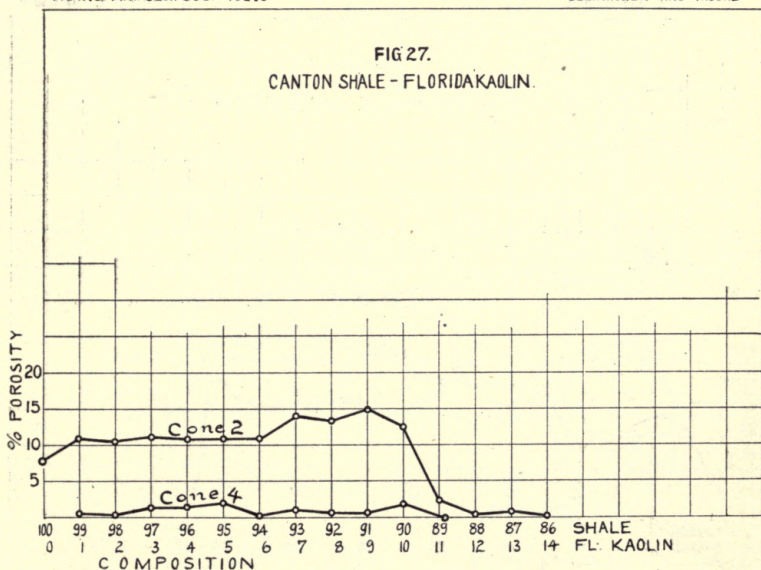
flint to Canton shale. Any addition of flint at once makes the clay more refractory until 11% have been added, when the drop occurs. At the last point the mixture seems to be but a trifle more refractory than the unmixed shale, Fig. 24. The rate of vitrification does not seem to be affected; if at all, it is in the direction of safer burning.

The Galesburg shale mixtures with flint show a decidedly lower vitrification range than the pure shales, and it seems, hence, that in this case flint acts as a pronounced flux, Fig. 25.

In the Crawfordsville shale the flint acts distinctly as a flux up to 5%, and at the same time it disturbs the rate of vitrification unfavorably, Fig. 26. Above 5% the refractory character of flint appears, which is maintained until 10% have been added. In this case also the rate of vitrification is changed in an undesirable manner.

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## ADDITION OF FLORIDA KAOLIN.

*Shales.* The first addition of 1% of kaolin to Canton shale in the Cone 2 curve produced an increase in porosity which then kept practically constant until 6% had been added. At this point another slight rise in porosity took place. Between 10 and 11% a sudden drop in porosity was observed, and it is evident that the kaolin in this proportion exerts a decided fluxing action, Fig. 27.

In the Crawfordsville shale a rise in porosity at 2% and a drop at 3% is observed. With 15% of kaolin a very decided decrease in porosity is noted corresponding to the drop with 11% Canton shale, Fig. 28.

In the Galesburg shale we observe (Cone 2 curve) a drop in the porosity for the addition of 1% kaolin, followed by a rise, after which the curve has a slight upward slope. At the highest percentage of kaolin added, 15%, the minimum point, if there is one, has not been reached, though the curve suggests its presence, Fig. 29.

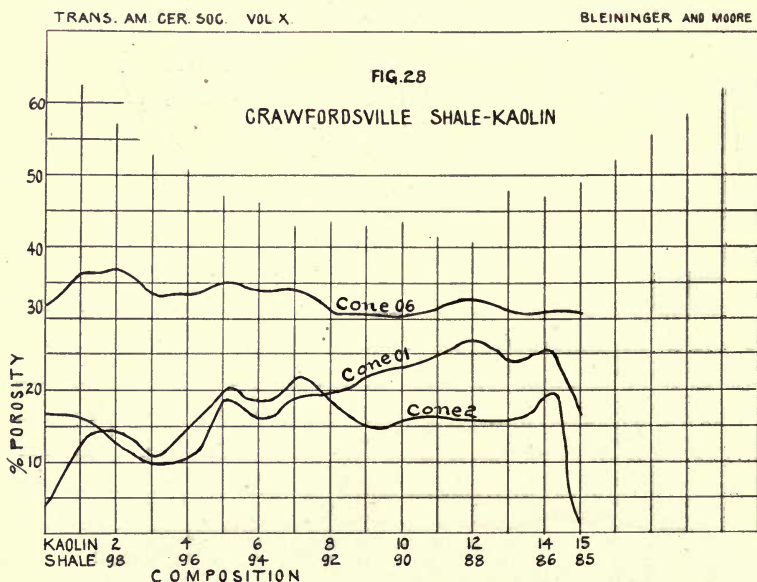
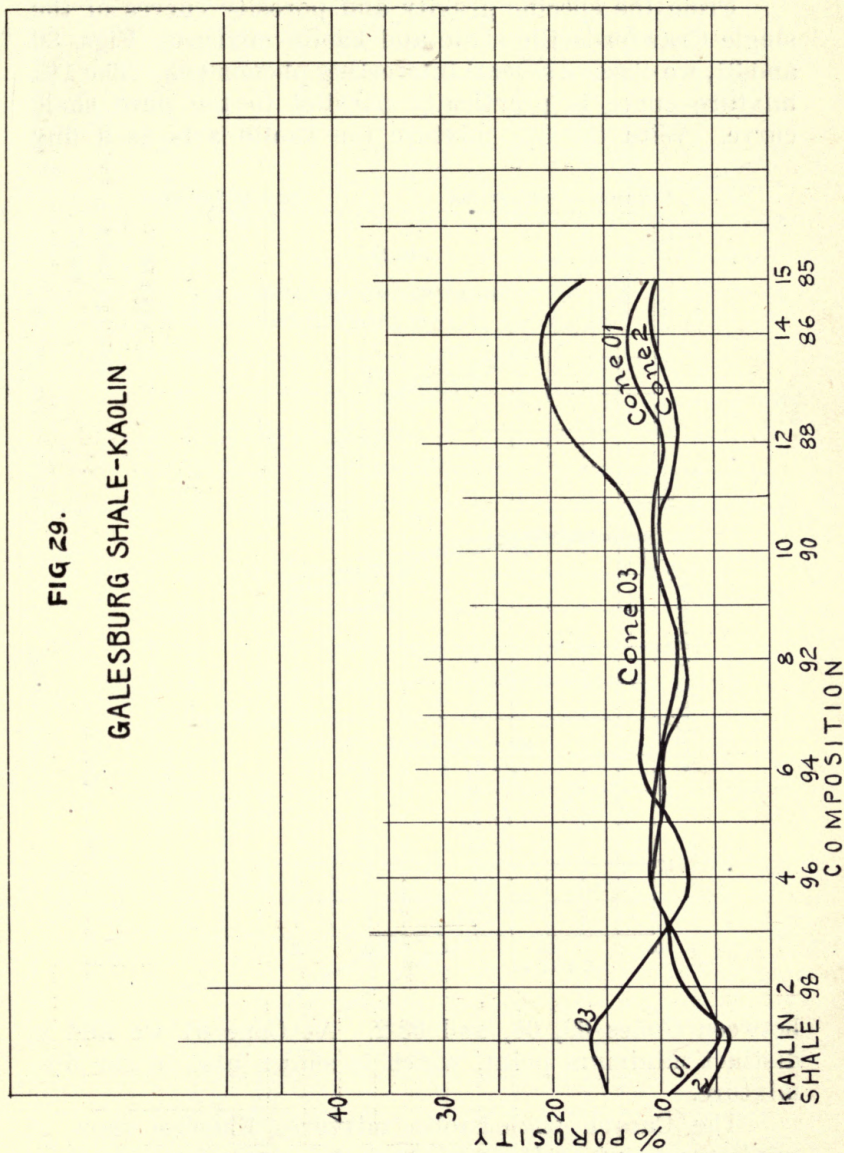
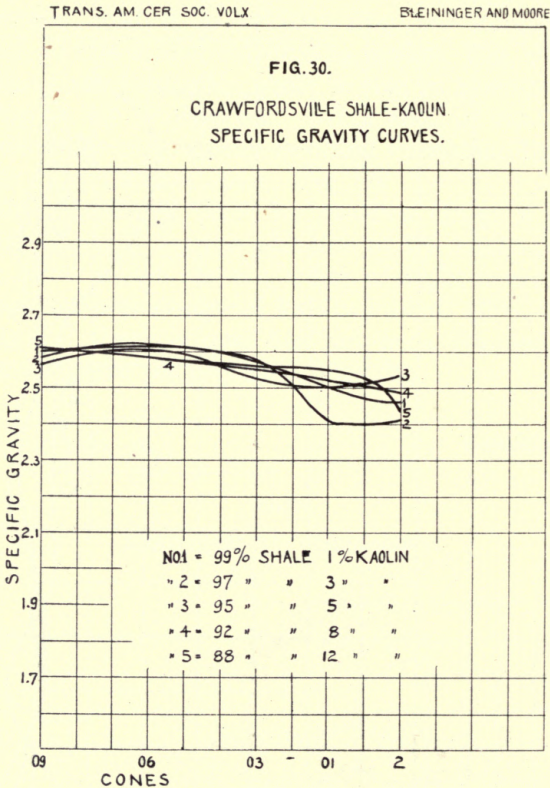


FIG 29.

GALESBURG SHALE-KAOLIN



From the specific gravity and porosity curves of the single Crawfordsville shale and kaolin mixtures, Figs. 30 and 31, we observe several interesting phenomena. The 1% mixture curve is practically parallel to the pure shale curve. With the 3% mixture the kaolin acts as a flux



between Cones 09, 06, and 03-2. At Cone 01 we find a distinct minimum point, which is shown also in the 5% mixture.

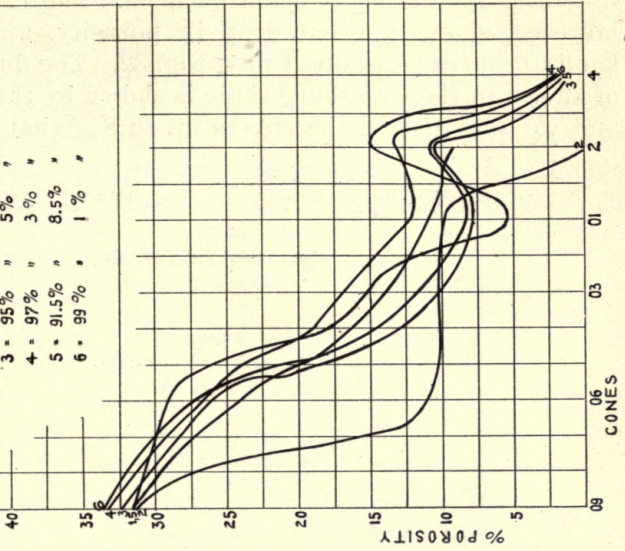
The Canton shale-kaolin mixtures likewise show a minimum point at Cone 01, and the curves indicate that up to about 10% the clay substance does not exert any



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FIG 32.  
CANTON SHALE - FL. KAOLIN.

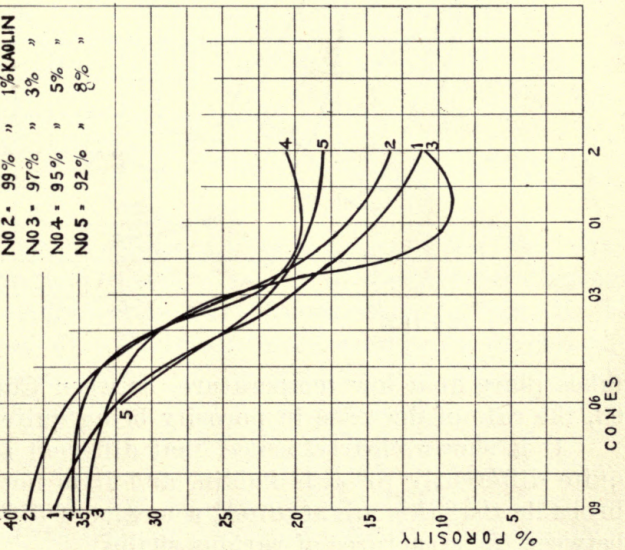
- 1 - 100% SHALE
- 2 - 89% " 11% KAOLIN
- 3 - 95% " 5% "
- 4 - 97% " 3% "
- 5 - 91.5% " 8.5% "
- 6 - 99% " 1% "



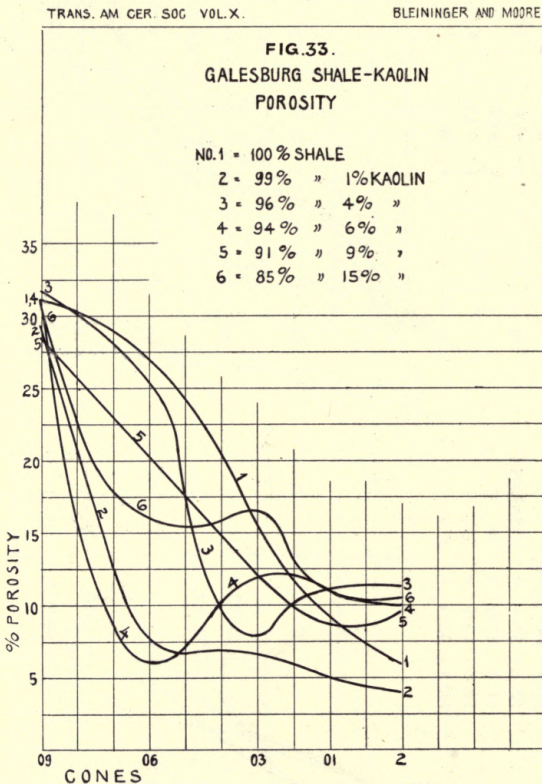
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FIG 31  
CRAWFORDSVILLE SHALE-KAOLIN  
POROSITY.

- NO 1 - 100% SHALE
- NO 2 - 99% " 1% KAOLIN
- NO 3 - 97% " 3% "
- NO 4 - 95% " 5% "
- NO 5 - 92% " 8% "



influence upon the clay below Cone 03. The 11% mixture, however, shows a great drop in porosity, and here the kaolin behaves as a potent flux, Fig. 32. The fluxing power of kaolin in the Galesburg shale is shown by the 1% curve, and we note also in the curves up to 8% that this action

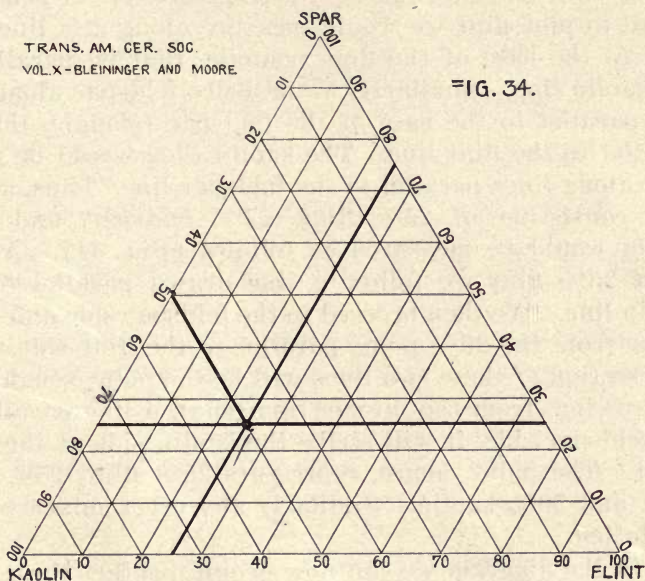


takes place at a low temperature, between Cones 09 and 03, the rate of decrease in porosity being quite steep.

It is shown clearly, hence, that different shales react quite differently towards kaolin, and it is not at all improbable that this might afford a means of differentiation between the structures of various shales.

ADDITION OF FELDSPAR-FLINT.

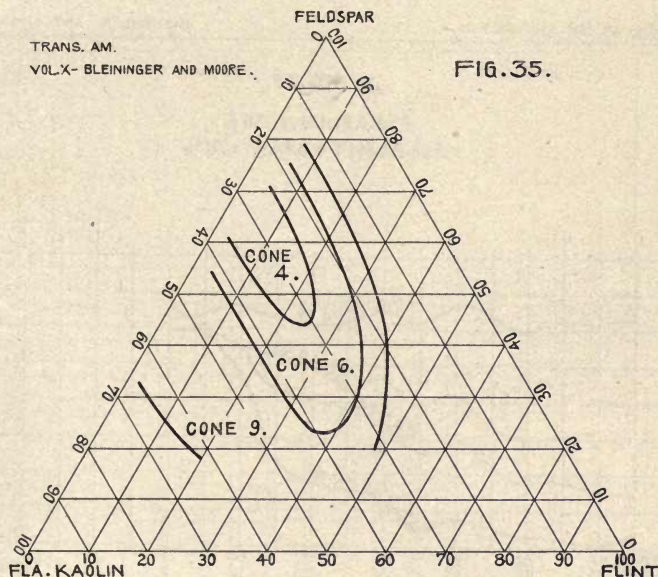
*Kaolin.* Mixtures of these three materials offer special interest to the clay worker inasmuch as they make up the bulk of our porcelain bodies. But the study of such a system becomes more complex, and hence the writers have resorted to the use of the triaxial diagram, which is a well known means of expressing three variable compositions



with the constant condition that the sum of the three components be equal to 100. The use of the triaxial diagram has been explained in our Transactions by Mr. H. E. Ashley (Vol. 7). To recapitulate briefly, let us call the lower left hand corner of the triangle, Fig. 34, the origin or 0 per cent of flint, then along the base of the triangle we measure the flint so that the right hand corner stands for 100% of flint. Continuing in the counter-clockwise direction we proceed to measure the feldspar along the right side of the triangle. This, of course, makes the 100%

flint corner equal to 0% feldspar, and the apex of the triangle then becomes 100% feldspar and at the same time 0% kaolin. The latter thus is measured along the left side of the triangle and the lower left hand corner becomes equal to 100% kaolin. We might thus represent to ourselves the diagram made up of three triangles, of which the apices are respectively 100% flint, 100% feldspar, and 100% kaolin. The base of each triangle then would equal 0% of flint, feldspar and kaolin respectively. If hence we desire to plot flint we would measure along any line parallel to the base of the flint triangle, that is, parallel to the kaolin line. Similarly, we measure feldspar along any line parallel to the base of the feldspar triangle, that is, parallel to the flint line. The kaolin then would be measured along lines parallel to the feldspar line. Thus, a mixture consisting of 25% flint, 25% feldspar, and 50% kaolin would be measured as follows (Fig. 34). At the point 25% flint we follow a line drawn parallel to the kaolin line. We then proceed to the feldspar side and draw a line from the 25% point parallel to the flint side. The intersection of these two lines will be the point sought, for on drawing, from the intersection point, a line parallel to the feldspar side, it will strike the kaolin side at the 50% point. The point, hence, represents 25% flint, 25% feldspar, and 50% kaolin. Similarly any other mixture may be plotted.

In the diagram we can now group together these mixtures, vitrifying at the same temperature by drawing lines connecting all mixtures whose vitrification point, that is, the point at which they absorb, not more than 1% of water is the same. For instance, by drawing a line around the area including all mixtures vitrifying at Cone 4 we have defined a thermal boundary, and the resulting curve we call the isothermal. By doing the same thing for the Cones 6 and 9 we obtain successive areas which increase in extent. This method, therefore, represents not only the compositions which may be expected to vitrify at a certain temperature from which the one most suitable for prac-

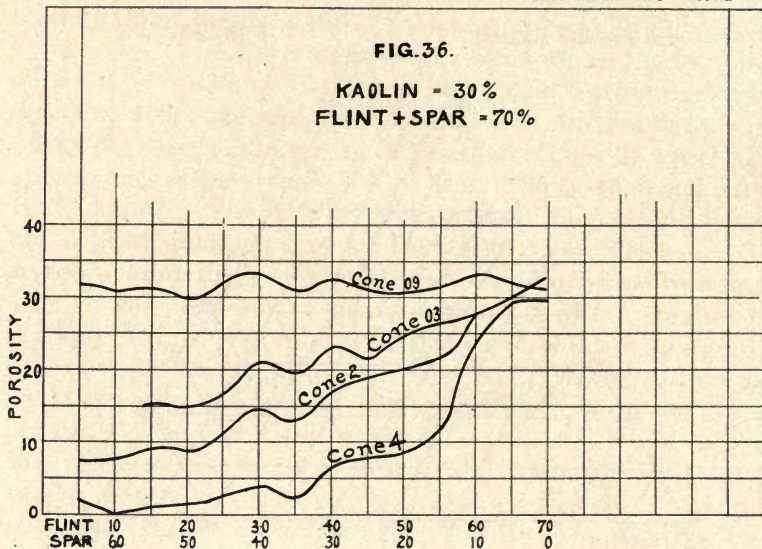


tical operation may be selected, but it also shows distinctly the intervals between the isothermals, thus expressing the range of the vitrification areas. Fig. 35 thus gives us a summary of the vitrification behavior of the system Florida kaolin-flint-feldspar, which needs no further explanation.

In Figs. 36, 37, 38, 39, 40, 41 we have mixtures of 30%, 40%, 50%, 60%, 70%, and 80% of Florida kaolin. In all the series excepting one, the 40% series, the porosity curves are fairly smooth. In this series two distinct maximum points are observed; one with 10% flint and 50% spar, the other with 50% flint and 10% spar. The cause of these two changes the writers do not venture to explain. In regard to the individual porosity curves of the kaolin-feldspar-flint series the rate of decrease in porosity becomes very sudden under two conditions, viz., in the kaolin-feldspar mixtures in the absence of flint, and in the mixtures containing but a small amount of flint compared with the amount of feldspar. This is more pronounced in the low kaolin series.

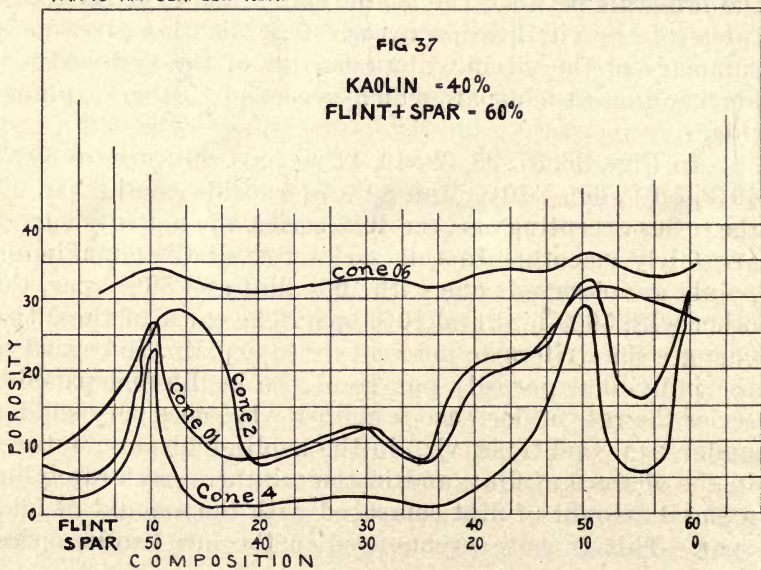
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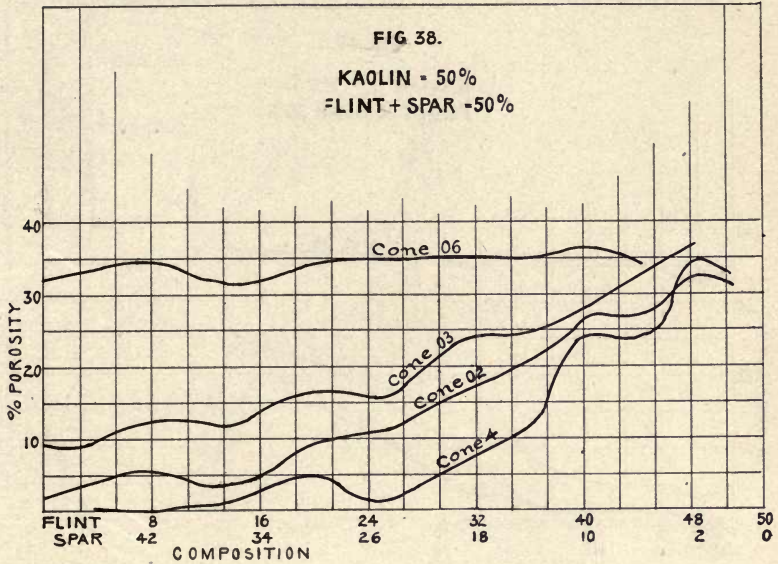
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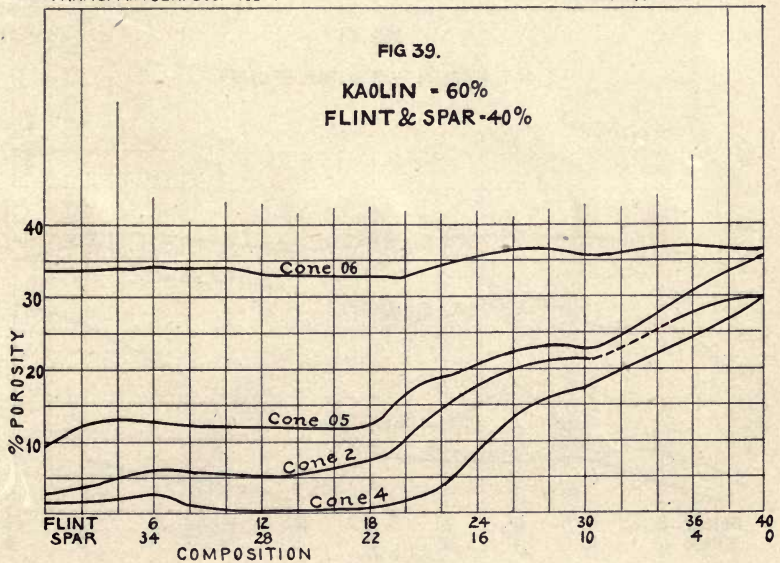
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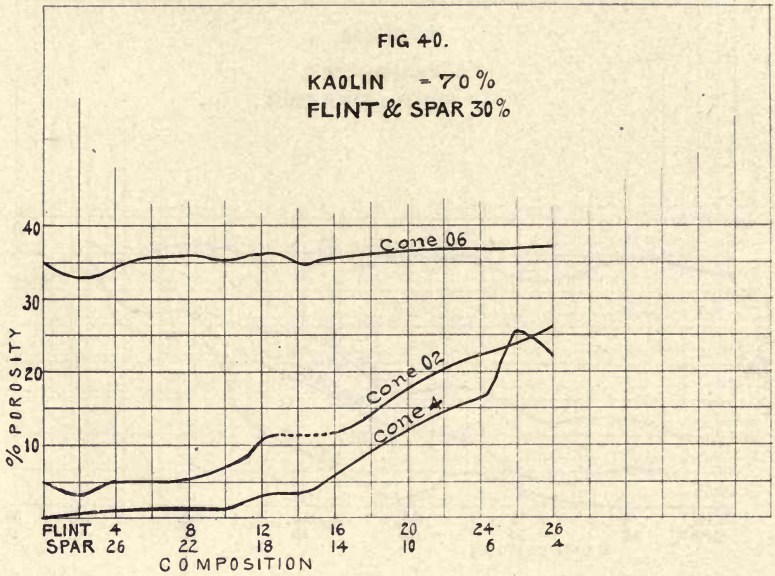
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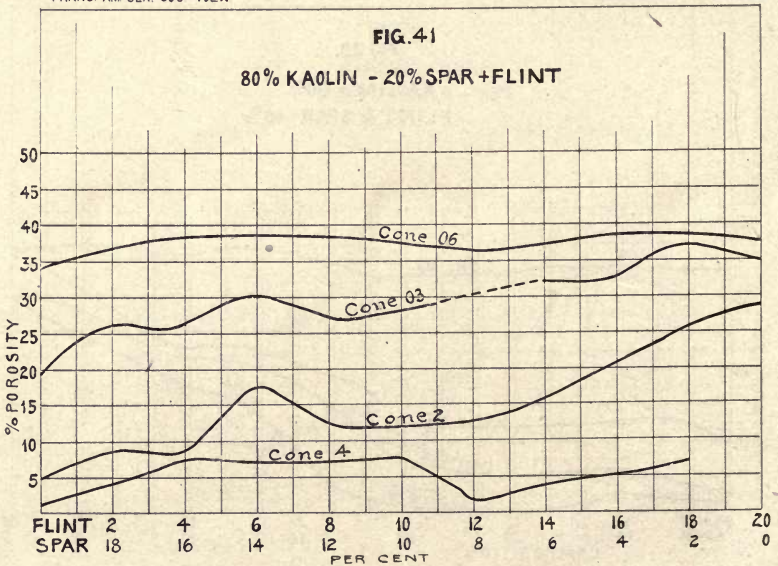
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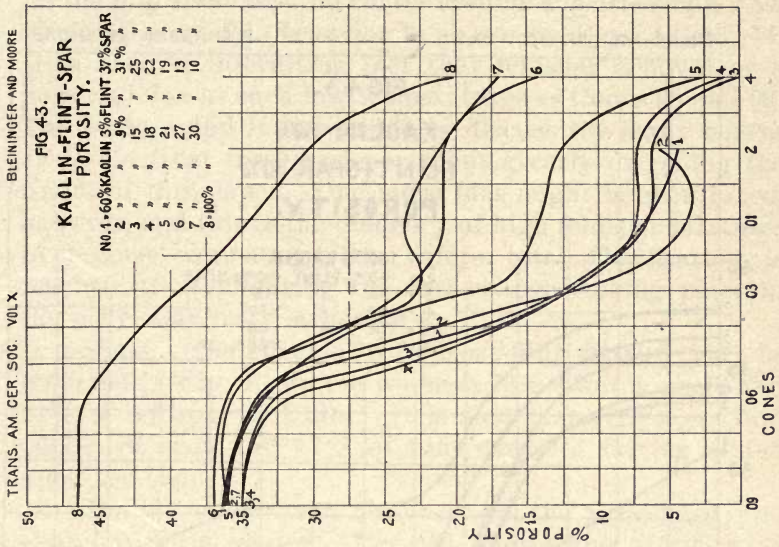
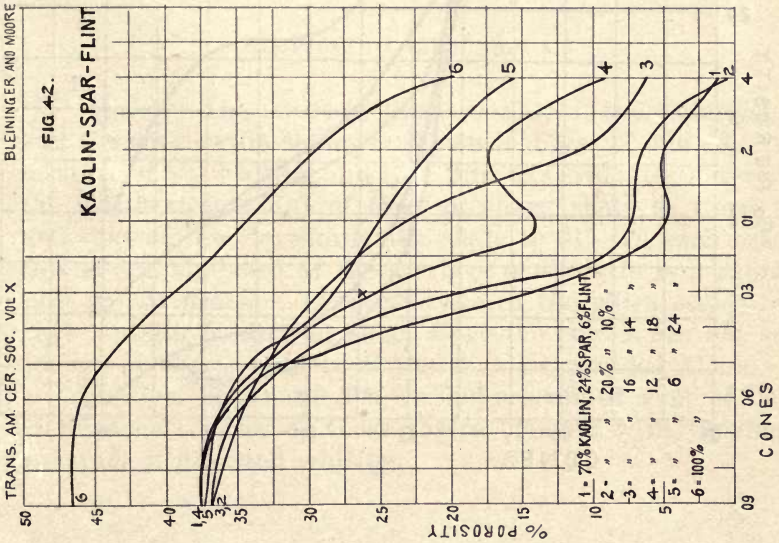


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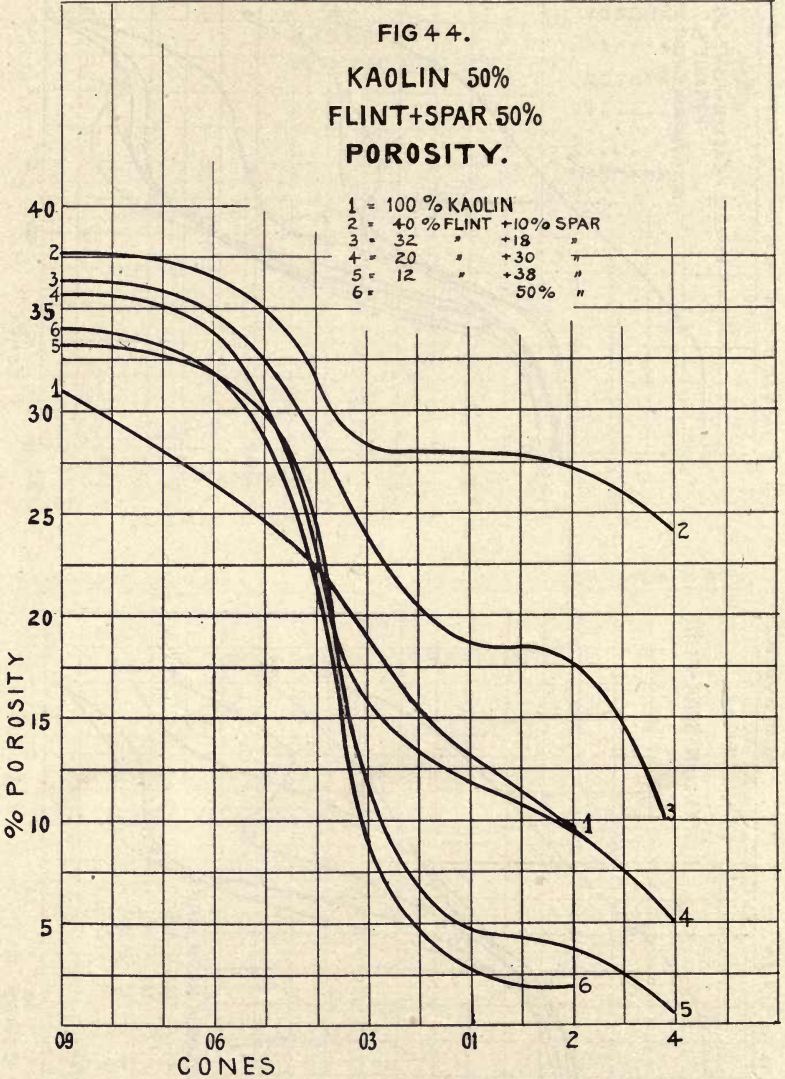






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As the flint increases the curves assume a gentle slope. An illustration of this behavior is shown by Figs. 42, 43, 44. It is also an interesting fact that feldspar behaves as a powerful flux at such low temperatures as Cones 06 and 03. The writers find it impossible to discuss the many curves available from these series without greatly exceeding the limits of this paper. One more fact might be mentioned, however, and this is the tendency of high feldspar mixtures to become vesicular, even before total vitrification is reached, thus obscuring the real changes taking place in the molecular body structure.

*Shale.* The effect of a feldspar-flint mixture may be observed in Fig. 45, where we have 76% Canton shale and 24% of feldspar and flint. It is seen that even a mixture of 7% of spar and 17% of flint exerts a fluxing action upon the shale.

Similar effects are observed on the Galesburg and Crawfordsville shales. Fig. 46 shows the vitrification of some Canton shale-spar-flint mixtures in which the fluxing effect of these components at Cone 2 becomes quite evident.

#### ADDITION OF LIME SILICA.

*Shales.* The effect of lime-silica upon the Galesburg and Crawfordsville shales is shown in Figs. 47 and 48. A mixture of 5% whiting and 15% flint has evidently lowered the vitrification point of the Galesburg shale to Cone 2 and that of the Crawfordsville shale to 01. In each case this is accomplished at the sacrifice of the safe to a rapid rate of vitrification. The presence of the silica seems to have a slight modifying effect since the curves are not so abrupt as they would be if the lime were added alone.

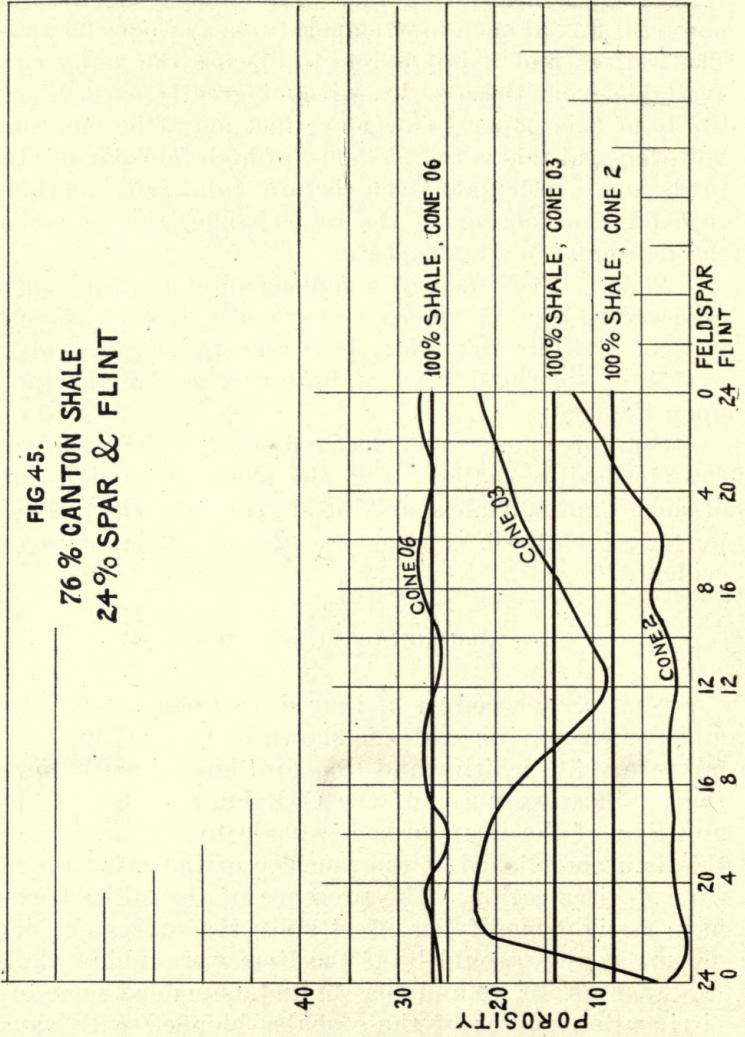
In Figs. 49, 50 and 50a we find assembled some of the vitrification curves of these shales blended with varying amounts of flint and whiting.

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FIG. 45.

76% CANTON SHALE  
24% SPAR & FLINT



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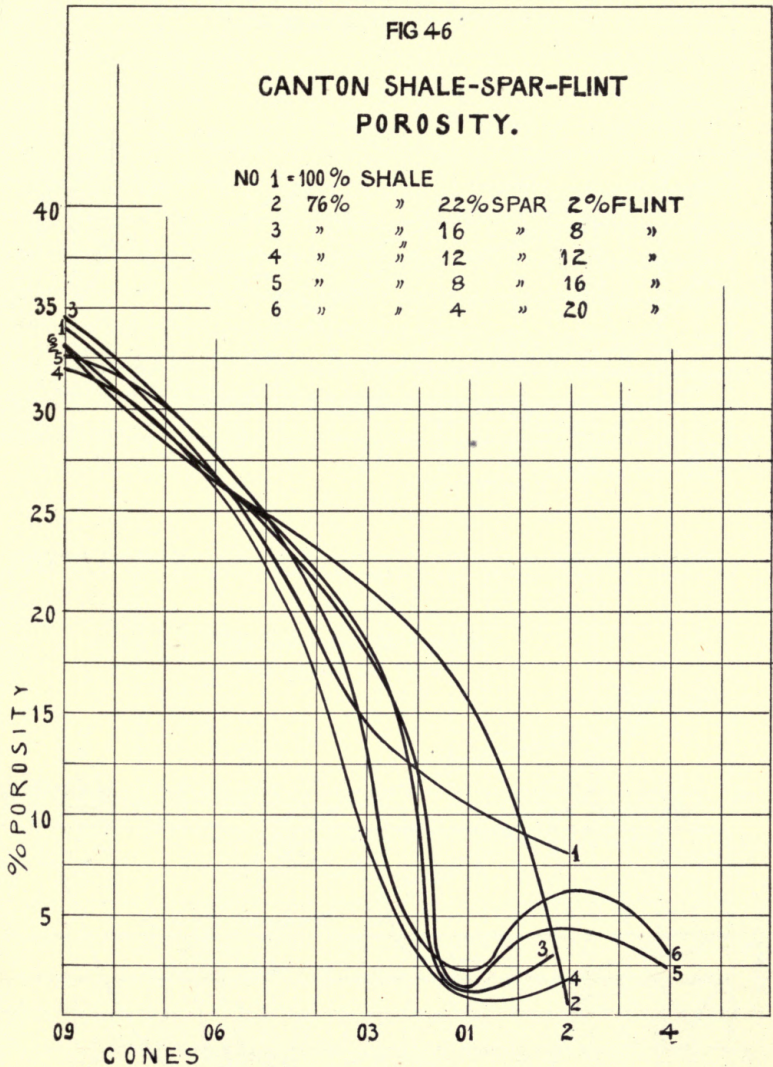
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FIG 46

CANTON SHALE-SPAR-FLINT  
POROSITY.

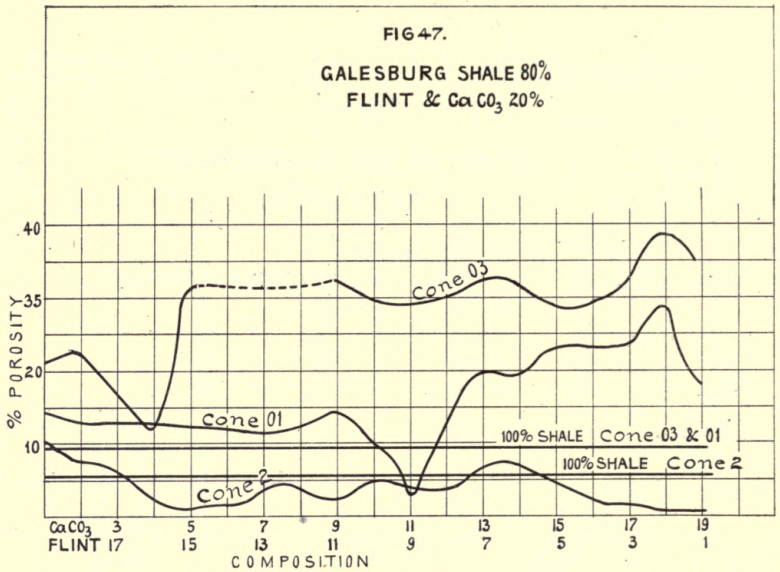
NO 1 = 100% SHALE

2	76%	"	22% SPAR	2% FLINT
3	"	"	16 "	8 "
4	"	"	12 "	12 "
5	"	"	8 "	16 "
6	"	"	4 "	20 "



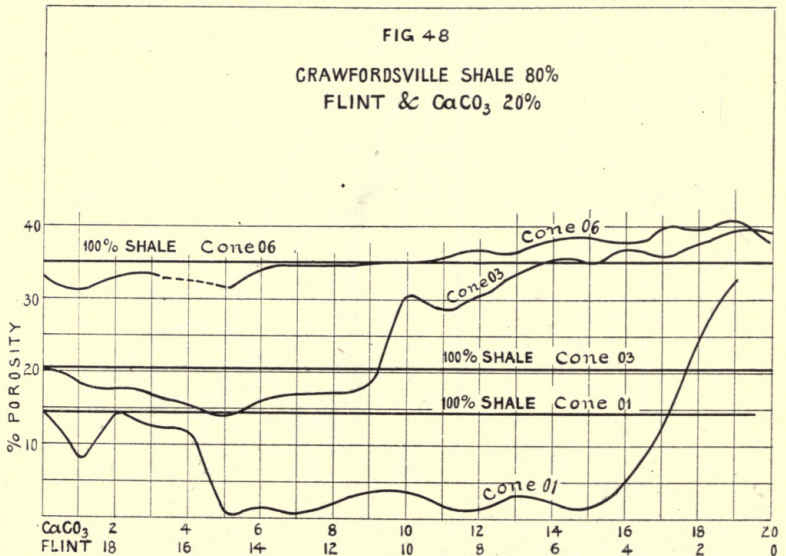
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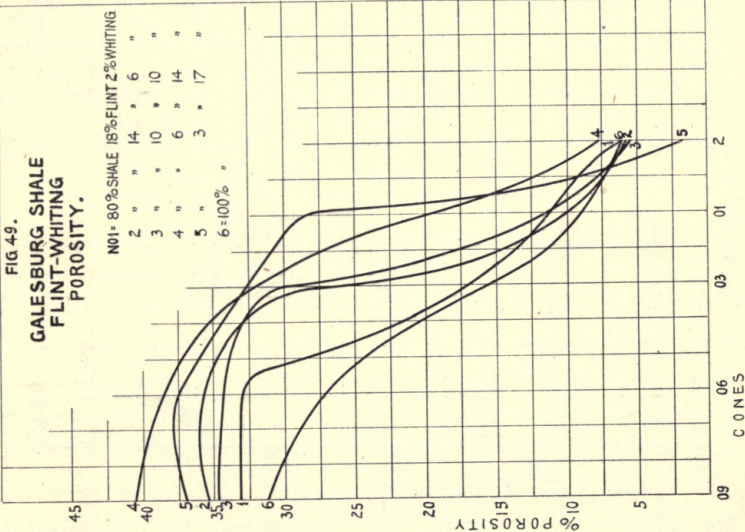
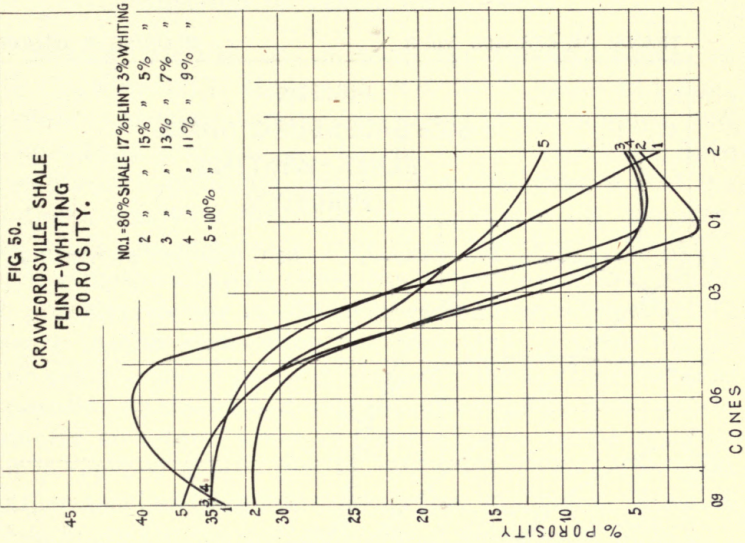
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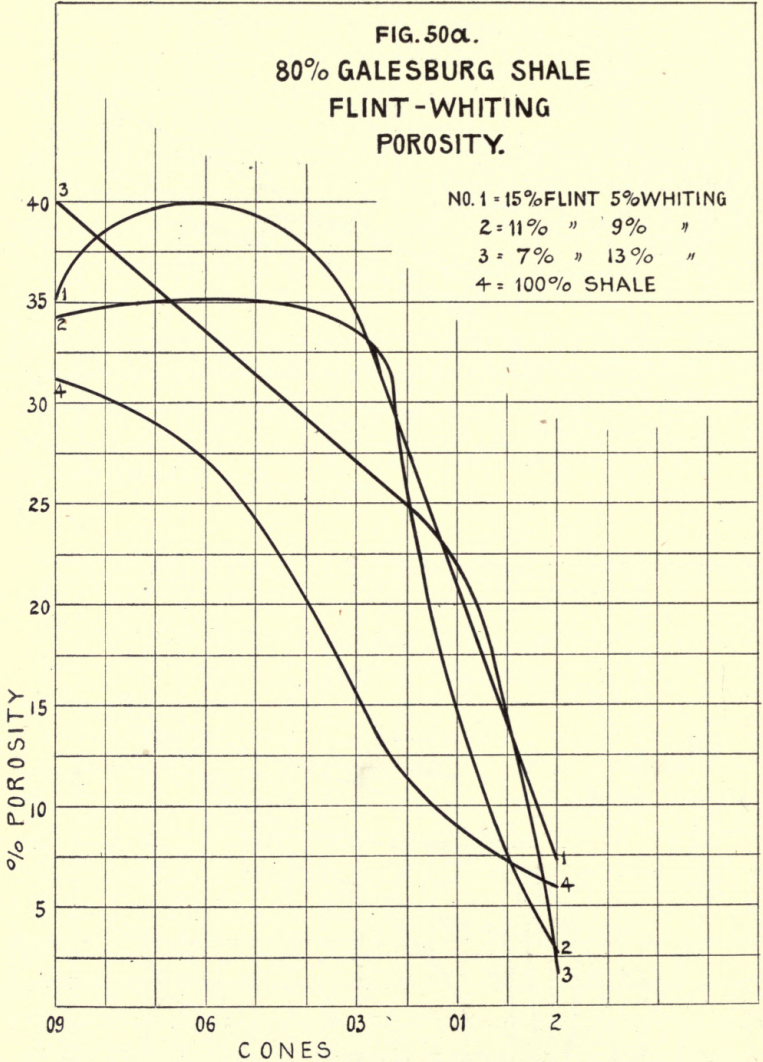
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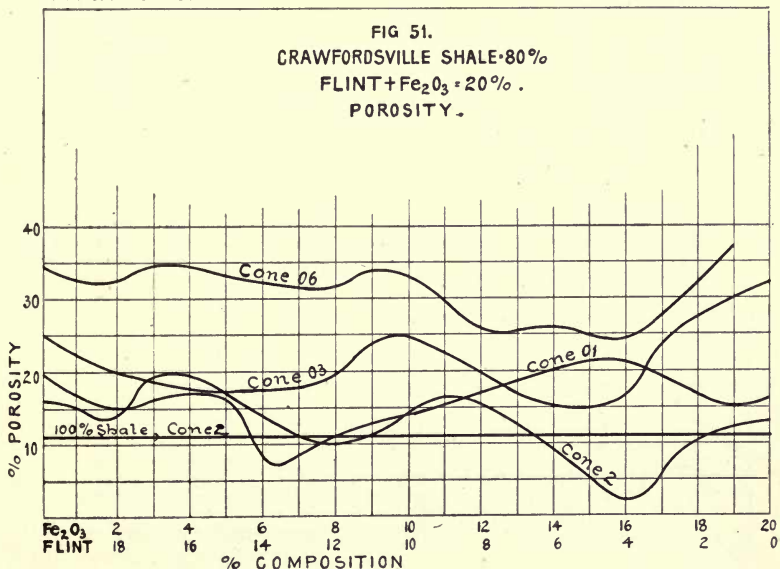
ADDITION OF FERRIC OXIDE-FLINT.

*Shales.* In Fig. 51, showing the porosity curves of 80% Crawfordsville shale and 20% ferric oxide and flint, we observe at once that the reactions appear complex, and by no means continuous. In the Cone 2 curve we have three distinct minimum points. We also observe that the reactions, whatever they may be, begin at a low temperature, since the curves lie very close together. With 6%  $Fe_2O_3$  even the Cone 01 curve has come considerably below the porosity shown in the normal shale at Cone 2. We observe in this connection the fact that at Cone 01 the shale shows a lower porosity than at Cone 2. This increase in porosity at the higher temperature appears to be due to vesicular structure, which is observed even before vitrification is reached at any point. With 16%  $Fe_2O_3$  the shale mixture reaches complete vitrification at Cone 2, at which temperature the normal shale has a porosity of 11%.

In a mixture of 75% Canton shale and 25% ferric

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oxide and flint, Fig. 52, we observe somewhat similar conditions. Complete vitrification is reached here as low as Cone 01, at which temperature the normal shale has a porosity of 12%. This point occurs with a mixture of 10%  $\text{Fe}_2\text{O}_3$ , 15% flint, that is, with a ratio of 2:3.

The Galesburg shale seems to behave more regularly than the preceding clays, and does not appear to produce the vesicular structure observed in the former. No decided change seems to take place at Cone 2 for the changes in the iron-flint ratio, Fig. 53.

The individual vitrification curves of these shales-iron-flint combinations are illustrated in Figs. 54, 55, 56.

Similar results have been obtained by Worcester in experiments involving the production of mixtures of red Bedford shale and ground Berea grit.

#### ADDITION OF FERRIC OXIDE-LIME.

*Shales.* Here we observe that in a mixture of 90% of Crawfordsville shale, 3%  $\text{Fe}_2\text{O}_3$  and 7% whiting have

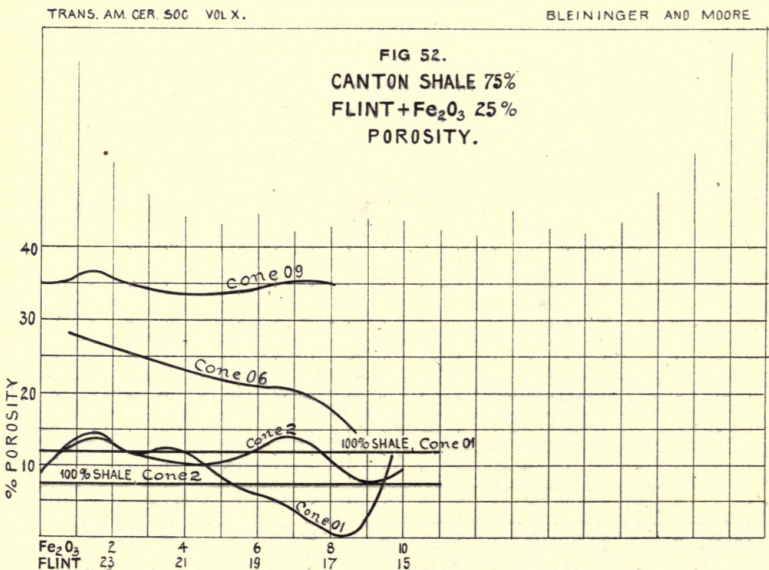
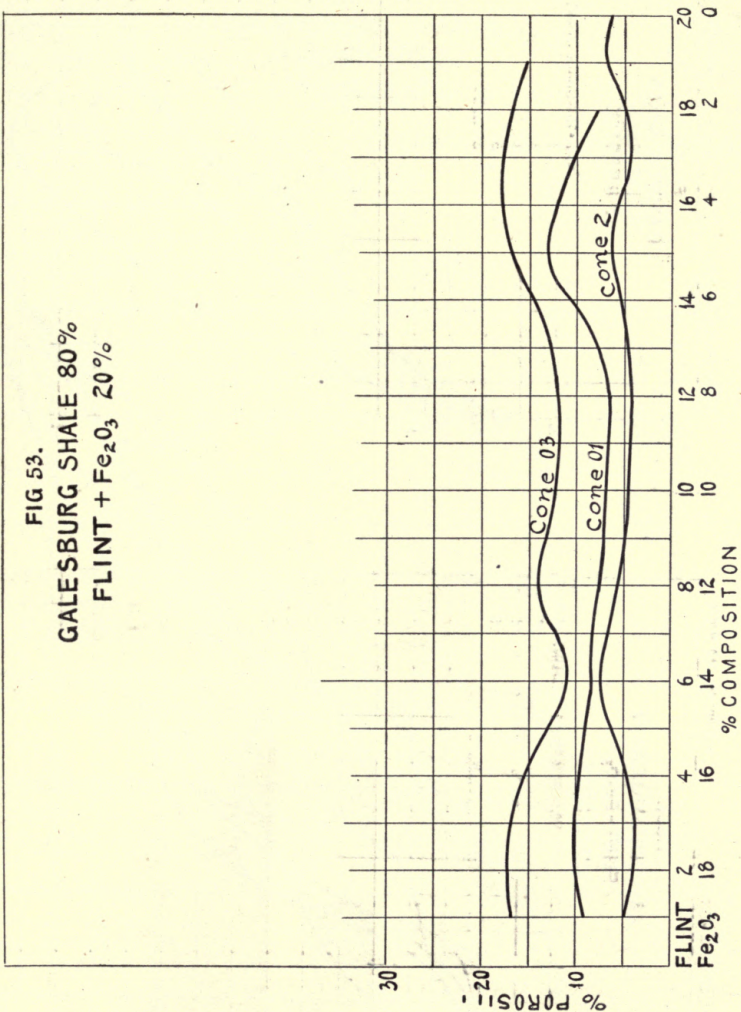


FIG 53.  
GALESBURG SHALE 80%  
FLINT + Fe<sub>2</sub>O<sub>3</sub> 20%



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FIG. 54.

## CRAWFORDSVILLE SHALE

FLINT -  $Fe_2O_3$ 

POROSITY.

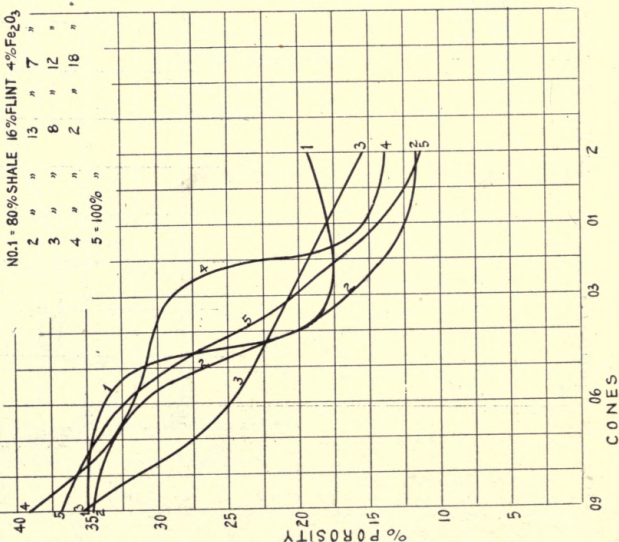
NO. 1 - 80% SHALE 16% FLINT 4%  $Fe_2O_3$ 

2 " " 13 " " 7 " "

3 " " 8 " " 12 " "

4 " " 2 " " 18 " "

5 = 100% "



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FIG. 55.

## CANTON SHALE

FLINT -  $Fe_2O_3$ 

POROSITY.

NO. 1 - 75% SHALE 23% FLINT 2%  $Fe_2O_3$ 

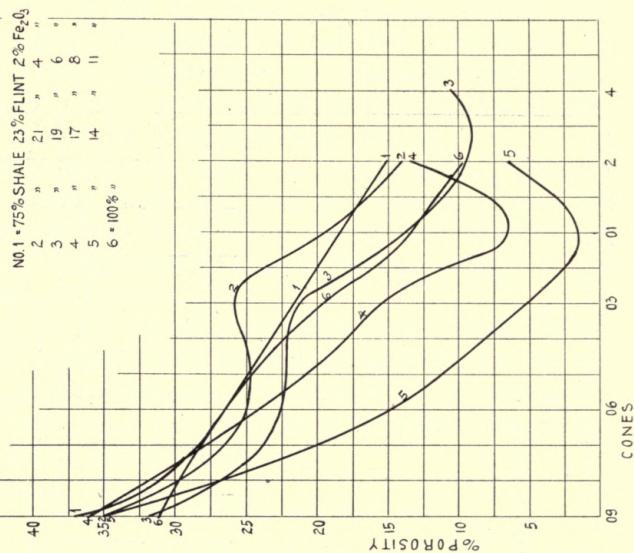
2 " " 21 " " 4 " "

3 " " 19 " " 6 " "

4 " " 17 " " 8 " "

5 " " 14 " " 11 " "

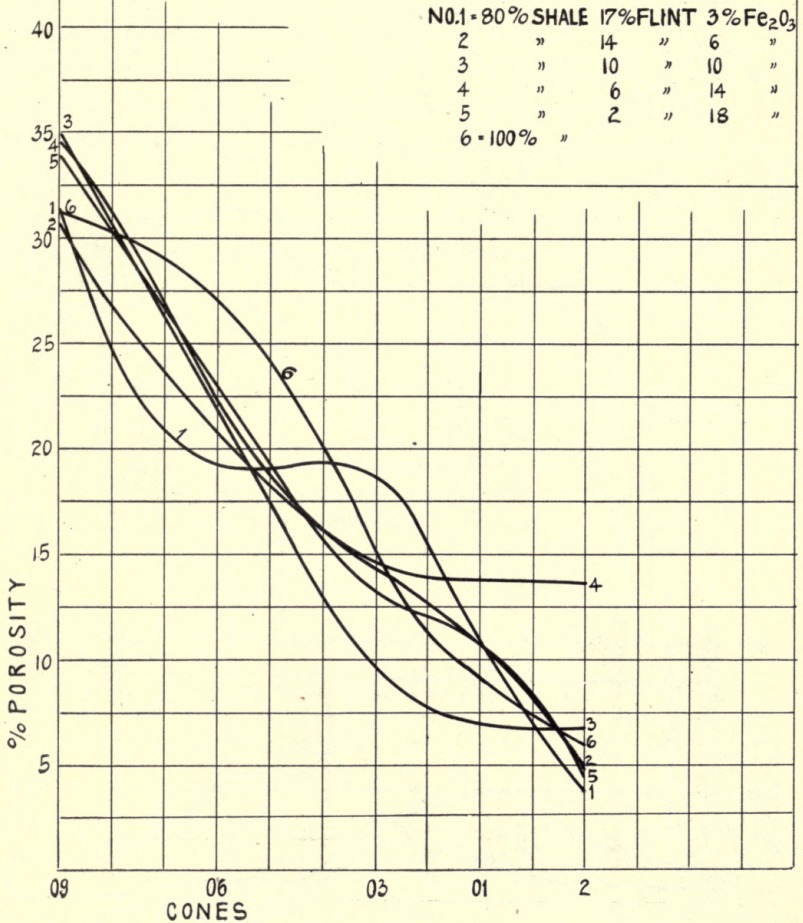
6 = 100% "



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FIG 56.  
GALESBURG SHALE  
FLINT-Fe<sub>2</sub>O<sub>3</sub>  
POROSITY.



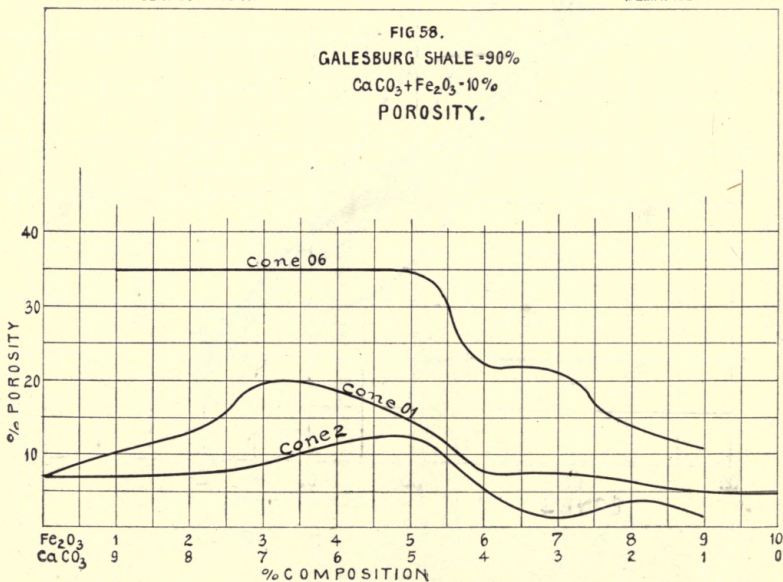
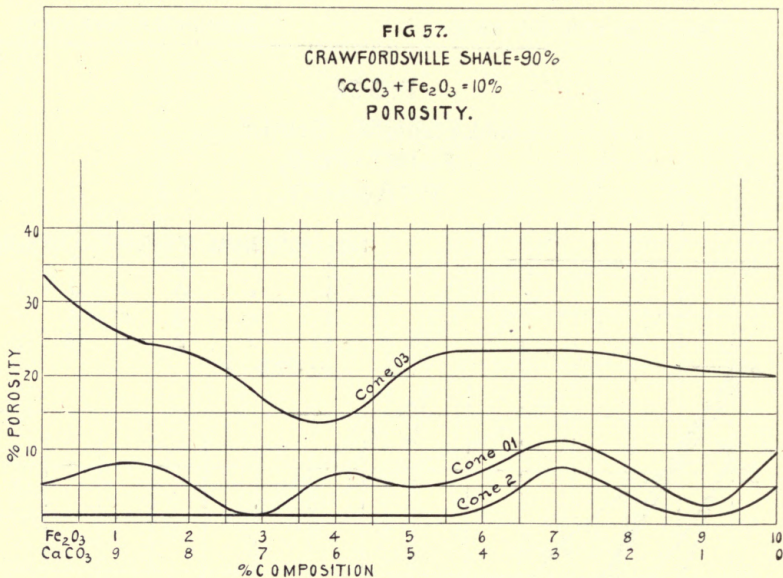
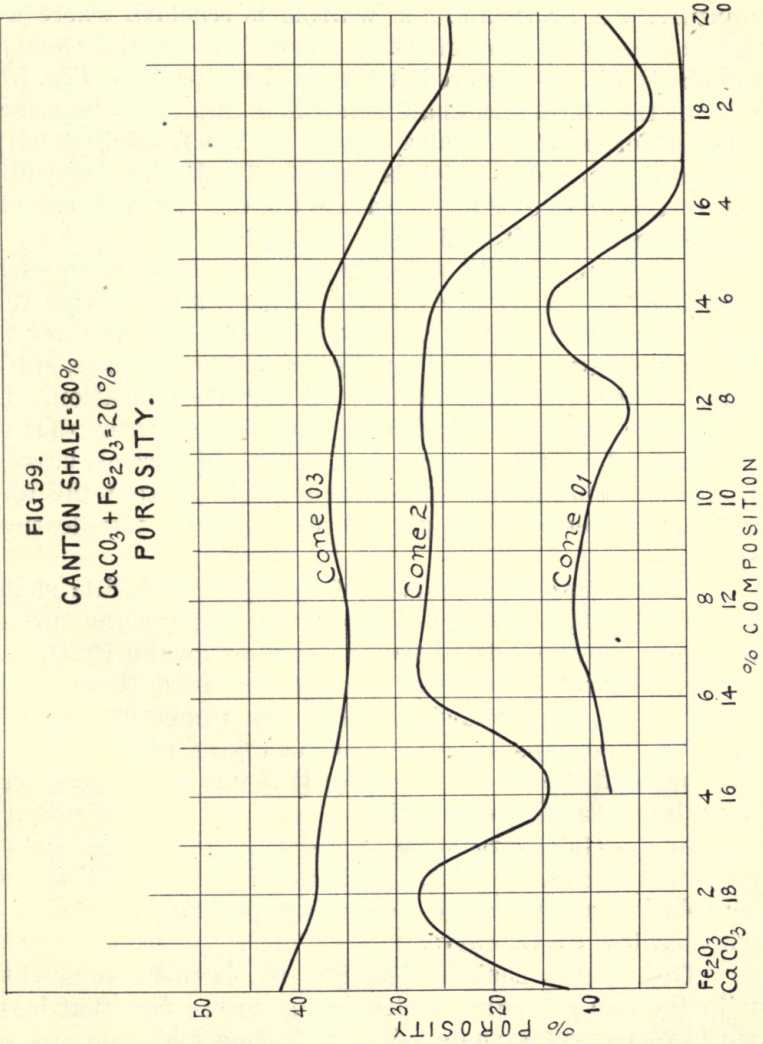


FIG. 59.  
 CANTON SHALE-80%  
 $\text{CaCO}_3 + \text{Fe}_2\text{O}_3 = 20\%$   
 POROSITY.



brought the vitrification down to Cone 01. Increase in ferric oxide causes the vitrification point to rise until the mixture, 9%  $\text{Fe}_2\text{O}_3$  and 1% whiting is reached, where we have a second minimum point. The Cone 01 and Cone 2 curves, it will be observed, are very close together, Fig. 57.

In the Galesburg shale conditions appear to be somewhat different and we have, within the range studied, only one minimum point which is close to 6%  $\text{Fe}_2\text{O}_3$ , 4% whiting in the Cone 01 curve. In the Cone 2 curve it has advanced to 7%  $\text{Fe}_2\text{O}_3$  and 3% whiting, Fig. 58.

The Canton shale seems to be more sensitive to such additions, as is shown in Fig. 59, where it appears that the shale has been rendered vesicular in structure at Cone 2. It is especially peculiar that this should be the case, since Cone 01 does not seem to have produced vitrification. It is possible that the vitrification range is so narrow that it was missed in the experiments. Yet this seems hardly probable. The natural conclusion would be that the formation of "blebs" took place before general vitrification set in.

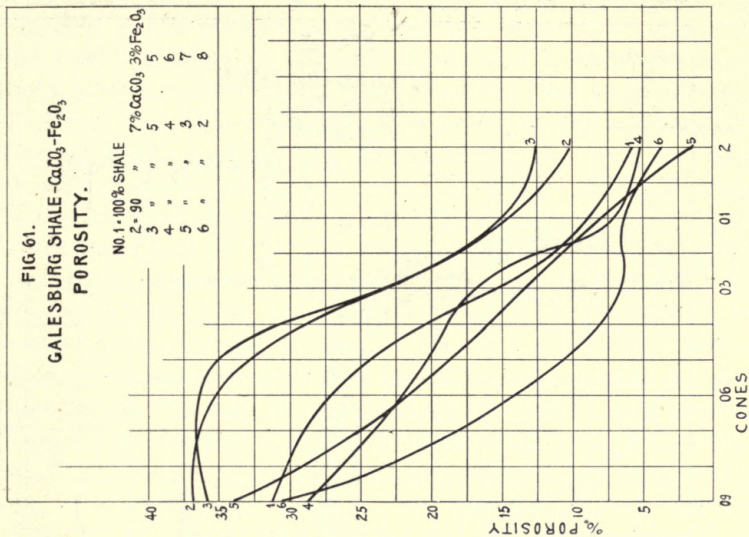
In the individual curves of the Crawfordsville shale series, Fig. 60, a gradual change in the slope of the curves is noted, which tends to become smaller as the  $\text{Fe}_2\text{O}_3$  increases. With the increase of the ferric oxide there is observed a peculiar retardation between Cones 06 and 03, indicating perhaps some phenomena taking place between the lime and the iron. Of course it is impossible to determine just what this change is.

In the Galesburg shale series, Fig. 61, the gradation on increasing the iron is smoother and not marked by the retardation noted above, excepting perhaps in the 4% whiting, 6%  $\text{Fe}_2\text{O}_3$  curve.

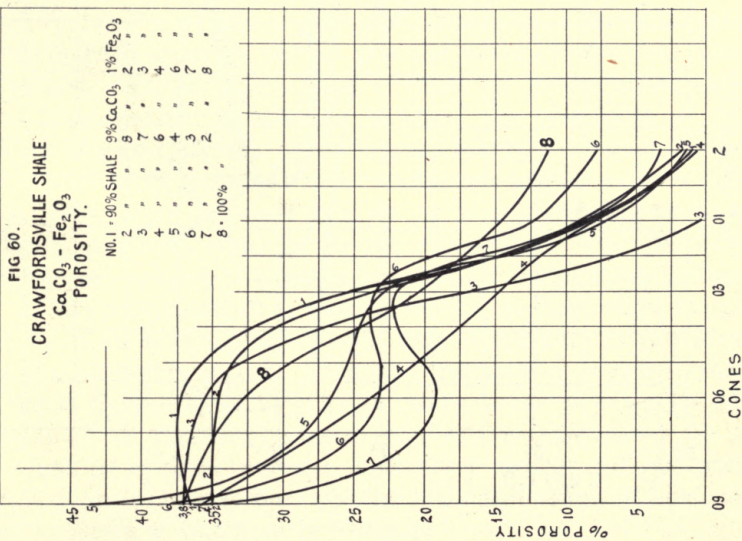
The Canton shale series, Fig. 62, is not comparable with the two preceding series, owing to the fact that here we have but 80% shale with 20% lime and iron oxide. However, some facts are brought out. First we have the change in slope with the decrease in lime, and second, we observe between Cone 01 and 2 a marked increase in poros-



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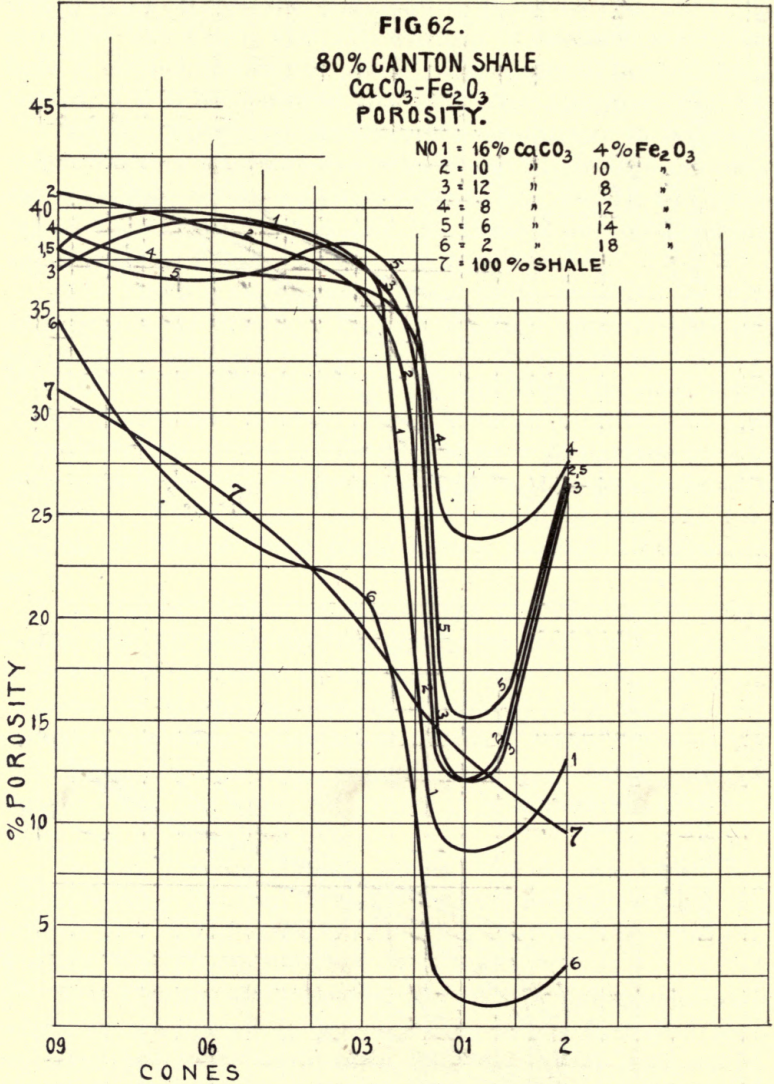


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ity which appears in every curve, the cause of which must be sought in the production of vesicular structure. It is possible that vitrification had set in at Cone 1, in which case it was missed, since no burn was made at this temperature.

From the data presented in this paper the writers believe that the method of determining the rate of the porosity changes affords a practical means of examining the vitrification phenomena not only of natural clays, but also of body mixtures. The porosity method is essentially a practical one, and where it is desirable to know the *molecular* changes, either physical or chemical, taking place, it must be supplemented by specific gravity curves representing the true specific gravities as determined by the pycnometer, under the special precautions advised in this paper. Unless these determinations are made with great care they are of little value, since the changes involved are frequently only of small magnitudes. The specific gravity curves employed in this paper, hence, are not close enough to admit of exact conclusions.

From the scientific standpoint, therefore, wherever the discussion of the molecular structure is involved, the true specific gravity curves are the main criteria of these changes. At the same time it must be remembered that the true specific gravity is in itself the resultant of the physical and chemical phenomena clearly indicated in the first part of this contribution, and cases might occur where the rate change becomes zero, owing to neutralizing factors. These, however, seem to be the exception. The porosity curves are subject to grave errors under certain conditions.

The maximum or minimum points, so important in the study of all fusion phenomena, may frequently be detected by the porosity curves. Their determination is more exact if fixed by the specific gravity curve, since practically all physical or chemical phenomena are accompanied by a change in specific volume, and since nearly all silicates (not containing any borates) on the application of heat, as far as known, increase in volume.

The use of reagents such as have been employed in this

paper seems to the writers to be of considerable value in bringing out and studying the differences in the chemical and physical structure of clays. Different clays will respond differently to the same reagent under the same heat treatment. To illustrate, every potter knows that there is a great difference between the behavior of English china clay and American kaolins. By heating each of these clays with, say, a mixture of 20% flint and 15% feldspar to several temperatures, different porosity curves will be obtained, showing the distinct characteristic of each type of material. It goes without saying that the reagent, whatever it may be, must be kept the same, both as to composition and fineness, just as the cement manufacturers and testers employ a standard sand for their purposes. This would mean the storing of a considerable amount of such a material. The preparation of the test pieces also should be done under uniform conditions.

Another extremely important factor is the heat treatment, which should be continued long enough to establish conditions of equilibrium and should be noted as closely as possible with reference to cone temperatures. That the heating should be the same in each case is self-evident, since we know that we are dealing with incomplete reactions which differ for different heat treatments.

In this connection the need of a really satisfactory small laboratory test kiln becomes very apparent, and this problem awaits solution.

As has been said before, for practical purposes the porosity curves are amply sufficient.

There can be no doubt but that we must approach the study of our clay bodies and mixtures along this line, and before definite laws can be laid down a great deal of work must yet be done. This field has been barely opened, but it is hoped that the function of the several substances studied will be indicated. What is needed most is the study of the simpler combinations.

In conclusion, the writers wish to express their indebtedness to Professor C. W. Rolfe for having granted

the funds and facilities necessary for carrying out this work.

#### DISCUSSION.\*

*Mr. Purdy:* This paper cannot be discussed at all adequately because of the mass of data presented. The curve form is probably the most lucid way of presenting data, but the mass of data is so confounding that you can not expect one to follow it in the short time which has been given it.

There were a few points though that I noticed as he went along; for instance, perhaps that iron did not seem to have acted as a flux, as we supposed it did, except in the role of a catalyzer. We noted the same thing last year in the study of the microscopic slides of burned shales, the iron separated out into definite crystals instead of combining with the silica. If iron combines with silica to any great extent it certainly would in a shale burned to a very dark chocolate color under both reducing conditions and great heat. Under each of these conditions the iron separated out into definite crystals. We have had data presented here today showing that the iron, instead of fluxing the clay, seems to have acted as a refractory agent, preventing the closing of the pores. The effect of iron on the specific gravity seems to be that to some extent, it holds it up, if it does not increase it. The same proved to be true with lime in large quantity. Lime in small quantities tends to decrease the density of clay by fusion, and hence a molecular arrangement of the fused constituent, and also by development of vesicular structure, but in excess of seven percent, it tends to increase the density of the mass. This is new to me, but I have no doubt it will be fruitful of new postulations when we come to study the curves.

It has been noted that sand added to shale increased

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\*This paper was not read nor presented in its entirety; such portion that was presented was given extemporaneously by Mr. Moore. Those whose discussed the paper have not had opportunity to see it as it appears above.—(Editor.)

its toughness when made into the form of brick and used as a paver. Sandy clays are as a rule better paving materials than those containing no sand; and sand—not pure quartz—added to clay increases its toughness. You cannot, however, add lake or glass sand and expect this constancy in specific gravity; nor can you expect this constancy in the porosity changes with increasing heat treatment, indicated by the curves just shown to us. You must have sand which is more or less combined, more or less in solid solution, as the chemists say, in order to have this steadiness of behavior in regard to fusion. The behavior of silica in decreasing the specific gravity without causing definite fluxing action is interesting. When a quartz crystal expands on heating it breaks, molecularly, and, at the same time, the molecules increase in volume. Notwithstanding the increased contact surface that follows as a consequence of this increase in volume, silica did not appear, in these experiments, to act as a flux.

I noticed that Cone 2 seemed to be the critical point in all mixtures, the point at which fusion begins to progress most rapidly. So Cones 2 and 3 can be said to be quite critical temperatures for most clays, if not for all clays and mixtures.

The behavior of kaolin when added to shale is most interesting. It seems to cause a fluxing action in small amounts and a refractory action in larger amounts. What is a flux? We have been used to classifying the bases, lime, magnesia, etc., as fluxes. We classify Cornwall stone and feldspar as fluxes, and clay and sand as refractories. We have an instance here of clay, a very refractory material, acting as a flux when mixed with shale. How can we harmonize this with our definition of a flux? It seems we ought to have a different definition from that we have been using.













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