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PROPERTIES OF SOME EUROPEAN PLASTIC FIRE CLAYS

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

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I. INTRODUCTION

In the manufacture of glass pots, tank blocks, glass furnace accessories, graphite crucibles, and similar refractories a certain amount of plastic clay is required for the purpose of bonding together the grains of calcined material, ground potsherds, and previously burned fire clay, which constitute from 50 to 60 per cent of the mixture used.

The requirements of such clays are very exacting and may be summarized as follows:

First, they must possess sufficient refractoriness to withstand the high heat of the furnaces, under the pressure of the liquid charge, without showing deformation; second, great plasticity and bonding power, making possible the cementing together of the grains of calcined material to a satisfactory compact mass; third, considerable mechanical strength and toughness, especially in the dried state; fourth, the quality of becoming dense at comparatively low temperatures in order to produce a structure impervious to the liquid glass or metal and resisting their corroding influence; fifth, the property of retaining a sound structure, free from vesicular development upon long-continued heating; sixth, the quality of resisting sudden temperature changes without checking or spalling; seventh, the property of drying and firing safely without cracking.

These requirements are severe and are possessed by comparatively few clays. The materials which have been found most satisfactory by years of practical experience are a number of European clays, principally those from Gross Almerode, Klingenberg, Schippach, and the Westerwald district in Germany, from Belforce and the Ardennes region in Belgium, and from the Stourbridge district in England. These clays possess the properties demanded of glass refractories to a marked degree. It would seem desirable, therefore, to investigate their properties in order that a basis of comparison be established, enabling us to estimate the value of domestic clays for the same purpose. Such results should be of particular importance at the present time when shipments of European clays are uncertain with the prospects of ceasing entirely.

II. NATURE OF PLASTIC FIRE CLAYS

1. STRUCTURE

We must at once eliminate from the discussion all kaolins and kaolinitic clays, which though refractory are lacking in plasticity and bonding power. This applies even to the secondary or plastic kaolins which occur interstratified with fresh-water limestones, sands, etc., in Georgia and the sandy deposits in Florida. All such clays possess a chalky, more or less friable, structure, and though they may be quite plastic they are lacking in bonding power and in strength when dried. sufficient for the present purpose.

The clays under consideration may exist in the soft or the indurated state. In the latter case they require grinding before they are able to assume the plastic state when admixed with water.

Good examples of plastic refractory clays in the soft state are the so-called ball clays of Tennessee and Kentucky in the United States and those from Devonshire and Dorset in England. The clays of this type are frequently high in carbonaceous matter and hence appear dark colored. Their plasticity is very great, their requirement of water of plasticity high, and their drying shrinkage marked. In the semidried condition they are tough, have a greasy feel, and when cut are found to possess a horn-like surface. They are apt to crack on drying when molded into larger masses, without the addition of nonplastic material. In the dried state they possess considerable mechanical strength.

The indurated or hard fire clays are usually of massive structure, show a characteristic conchoidal fracture, and slake down to a plastic mass when weathered. They often show slickenside surfaces. Grinding of the unweathered material must be invariably resorted to before it can be worked into a plastic mass with water. Considerable differences exist as to the readiness of slaking. Carbonaceous matter is invariably present in such clays and seems to be intimately connected with their nature. In certain cases the fatty character of the clays may be directly due to this constituent. Addition of caustic soda seems to saponify the organic constituents, forming salts of the fatty acids. In many clays the organic matter may be present as hydrocarbons. It is noted also in connection with clay deposits occurring beneath lignite beds that the part closest to the coal and highest in carbon possesses the greatest degree of plasticity. It is not unlikely that the organic matter may be closely associated with the difference between these clays and the kaolinitic materials. A dense, quite impermeable structure is characteristic of these clays. Their specific gravity, determined upon dried lumps, in the natural state, is considerably higher than that of the "fatty" alluvial and surface clays and affords a valuable distinction. Their compactness, therefore, is an essential condition.

The presence of iron pyrites is common with many of these clays. The occurrence of this mineral in appreciable quantity destroys their value for the purposes under discussion.

2. PLASTICITY AND BONDING POWER

Plasticity is the property of clays assumed by them when mixed with water and represents that condition in which they may be molded without suffering subsequent deformation. It is a condition made possible by the dispersed state of the hydrous aluminum silicates, known under the general name of clay substance. A certain portion of most clays is in such a finely divided state that the particles assume the properties of a suspensoid colloidal system. These fine particles have been estimated to possess a mean diameter of from 0.005 to 0.003 mm. According to the amount of the dispersed matter, the degree of dispersion, the nature of the fine particles and their compactness, the varying degrees of plasticity are produced, ranging from the strongly to the feebly plastic materials. Organic colloids and electrolytes appear likewise to influence this property to a very considerable extent.

The above statement that the cause of plasticity is to be sought in the dispersed state of the mineral particles is now generally accepted as being the most satisfying one. It must be considered a state rather than a particular kind of matter, though it must be realized that the latter point is of considerable importance. Thus, barium sulphate, usually crystalline, may under certain conditions form a colloidal, plastic substance. It is not to be supposed, however, that it would show the same degree of plasticity shown by the complex aluminum silicate, known as clay substance, which by virtue of its complex constitution, its content of OH groups, and slight solubility in water would be more inclined to be stable in the noncrystalline state. No entirely satisfactory measure of plasticity has yet been devised and some of the tests are of an indirect character. The Zschokke[1] method of determining the tensile strength and deformation of the clay in the plastic state, that of Grout[2] and of Emley,[3] involving the measurement of deformation under compression, seem to be the most promising. The latter two methods correlate the pressure required to produce fracture of the test cylinders and the deformation. One of the important difficulties is the consideration of the proper water content; that is, normal consistency. Fortunately, an experienced operator is able to detect the best working consistency with a considerable degree of accuracy. Mechanical tests, such as the application of the Vicat needle, have not been more satisfactory than the estimation by the "feel."

It is generally known among clay workers that the very plastic clays require more water in order to assume the best working consistency than the leaner ones, in agreement with the fact that the

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[1] Bull. Soc. d'Encour., p. 103, pp. 619–658, 1902; Baumaterialienkunde, 7, pp. 149–152, 165–170, 1902.

[2] Geol. Survey of W. Virginia, III, p. 40.

[3] Trans. Am. Ceram. Soc., 17, p. 612.

former represent a greater degree of dispersion and hence more surface to be coated with a film of water. Excessively plastic clays may thus be clearly distinguished from those of normal properties by their high water content. The shrinkage of clays upon drying parallels the content of water of plasticity, for the greater the latter the more contraction is bound to take place. Hence, both the content of water and the drying shrinkage are indirect means of estimating the plasticity.

Atterberg[4] makes use of this factor by determining the amount of water contained by the clay in two stages, at the "rolling" and at the flow limit. The first is that stage at which the clay can just be rolled into threads, a point quite sharply defined; the second represents the state in which the clay can be made to flow on a concave smooth surface which is subjected to rapid impacts. The difference in the contents of water represents the so-called Atterberg plasticity factor. The greater this value the more plastic is the clay supposed to be. Applied to American clays, Kinnison[5] has found it necessary to correlate the Atterberg number with the total content of water of the clays when they are in the plastic state. The results of this worker are compiled in Table 1, which gives the limiting values for the different classes of clays.

TABLE 1

Material	Atterberg plasticity factor	Minimum water of plasticity	Maximum water of plasticity
Kaolins:		Per cent	Per cent
Primary	6. 5–10	27	31
Secondary	13 –16	25	31
Ball clays	16 –29	29	35+
Plastic fire clays	8 –10	15	19
Shales	7 –12	17	22

According to the Atterberg factor the wider the range in water content between the two limits the more plastic should be the clay. In general, this agrees with practical results. Thus, sandy clays possess but a narrow range and the excessively plastic clays a very wide one. In this connection it might be stated that excessive plasticity may be as detrimental as low plasticity, inasmuch as the water-laden structure of such materials does not result in the desired strength besides giving rise to difficulties in drying and burning.

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[4] International Reports on Pedology, 1911; C. S. Kinnison, Bureau of Standards, Tech. Paper No. 46.

[5] Loc. cit.

Of the indirect methods that of determining the tensile strength of the clay in the dried state seems to be used most commonly though it is being replaced more and more by the transverse test of dried bars. In general, it is undoubtedly true that the mechanical strength of the dried clay is, in a way, a measure of the plasticity, since this is known to be the case for the strong ball and bond clays. There are experimental difficulties to be met, however, due to the cracking and checking of the clays in drying and to strains set up which give erroneous results in the strength tests. Cracking may occur even in the most carefully conducted drying process. For this reason it has been suggested that the clays be intimately mixed with 50 per cent by weight of standard Ottawa sand and these errors avoided.[6] In this manner the results would be indicative also of the bonding power of the material, viz, its capacity to cement together a given volume of nonplastic particles and to produce a body of the required mechanical strength. The error incidental to strength tests of dried clay is quite large and it has been the practice in the Pittsburgh laboratory of the Bureau of Standards to take as the reported result the average of 20 determinations. In Table 2 the results of a large series of tests are compiled giving the tensile, compressive, and transverse strengths of dried clays, without and with the admixture of standard Ottawa sand in the proportion of 1 : 1, by weight.

TABLE 2

[Data shown in pounds per square inch]

Material	Tensile strength		Compression strength		Modulus of rupture	
	Without sand	With sand	Without sand	With sand	Without sand	With sand
English ball clay (a)	210.0	190.0	1148.0	777.0	558.0	330.0
English ball clay (b)	161.0	152.0	806.0	623.0	438.0	303.0
Pennsylvania No. 2 fire clay	155.0	113.0	631.0	476.0	520.0	216.0
English ball clay (c)	154.0	158.0	1056.0	556.0	508.0	319.2
Georgia kaolin (a)	147.0	110.5	455.0	390.0	325.0	210.0
English ball clay (d)	135.0	127.5	565.0	464.0	375.0	242.0
Tennessee ball clay	125.0	124.0	633.0	489.0	380.0	243.0
Georgia kaolin (b)	109.0	97.5	519.0	559.0	269.0	182.0
Florida kaolin	104.0	54.0	539.0	286.0	239.0	122.0
North Carolina kaolin	56.5	34.9	349.0	168.0	166.0	82.0
English china clay (a)	33.2	26.1	228.0	172.0	98.0	53.0
English china clay (b)	29.6	28.8	205.0	164.0	74.0	56.0
Ohio No. 3 fire clay	....	150.4	954.0	553.0	484.0	280.0
Ohio shale	136.0	101.0	636.0	403.0	311.0	199.0
West Virginia shale	187.0	77.0	748.0	407.0	403.0	178.0

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[6] Bleininger and Howat, Trans. Am. Ceram. Soc., 16, p. 273.

Another indirect test for plasticity is also the so-called slaking test, in which a cube of dried clay is immersed in water and the time of its disintegration noted. Clays of the kaolin type will slake almost instantly, and as the character of the materials becomes more and more of the strong, tenacious type the time required to break down the specimen will increase in a very decided manner. Very strong clays resist the slaking action of the water for a considerable period. This test is practiced by German glass pot makers and may be modified by intimately blending with the clay, in the dried state, potters flint in the proportion of 1 : 1 by weight and molding into seven-eighths-inch cubes. After drying at 110° C the cubes are immersed in water at room temperature and the time of their breaking down noted.

3. FINENESS

The fineness of grain of clays is closely associated with plasticity, as has been mentioned before. Of greatest interest in this connection is a knowledge of the quantity of finely dispersed matter which contains practically all the clay substance and in addition some of the nonplastic constituents, quartz and feldspar. The apparatus used for this purpose is either of the elutriating or the sedimentation type, employing water as a medium. In the first kind of separating apparatus several arbitrarily classified groups of sizes of grain are removed by means of definite velocities of the water current. The first group separated comprises the particles of the smallest size which can be removed under conditions possible of control. Seger[7] has adopted for this group a velocity of 0.18 mm per second, which corresponds to a maximum size of 0.01 mm. Undoubtedly this represents the most important separation, as it includes all of the clay substances. It would be erroneous, however, to consider this fraction as consisting only of clay substance, as undoubtedly fine quartz and feldspar are invariably present. The remaining material must be considered granular in character since it is lacking in real plasticity. The other separations advocated by Seger are silt, 0.025 to 0.01 mm; current velocity 0.7 mm per second; dust sand, 0.04 to 0.025 mm, 1.5 mm per second; fine sand, 0.333 to 0.040 mm, and coarse sand larger than 0.333 mm. The Schoene elutriating apparatus is probably the best known of the devices proposed for this purpose. It consists of a glass cylinder, provided with a piezometer, and

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[7] Gesammelte Schriften, p. 33.

is supplied with water from a container, under a constant head. This simple device can be made to do good work provided the temperature of the water is kept as constant as possible and either rain or distilled water is used in its operation. It is desirable also to deflocculate the clay sample at the beginning of the run with caustic soda or to maintain a small alkali content in the wash water.

Another elutriating apparatus sometimes used for this purpose is that proposed by Schulze. Here the flow of water is kept constant and the several desired velocities are obtained by using three or four increasingly large cylinders. The material is placed first in the smallest can, in which the highest velocity is maintained, and is then carried into the larger ones. Since the velocity is constant in each can a definite fraction will be thrown down in the conical bottom of each. The comparatively large areas of the separating cans and the size of the latter cause certain irregularities in operation and hence variable results, which, however, can be partly neutralized by the use of larger samples of material. The Schulze apparatus is easier to operate than the Schoene and is more suitable for industrial control where approximate results suffice.

4. COMPOSITION

The chemical and with it the mineral composition of the plastic fire clays under consideration is obviously of fundamental importance; but it is influenced and modified so largely by physical conditions that as a guide in the selection of suitable clays it is of secondary service. This is illustrated by the fact that we have in the United States a large number of clays practically identical or closely approaching the chemical composition of the best-known European bond clays but which fail completely in satisfying the requirements. We are compelled, therefore, to assign to chemical composition a secondary value. This does not mean, of course, that the composition is to be entirely neglected. It must always correspond to that of refractory clays. Any excess of fluxes would evidently render the material valueless, since refractoriness is one of the conditions to be met. The fact to be realized is that it fails to differentiate between the several types of fire clays, all of which are sufficiently refractory for the purpose.

In studying the clays of this type a knowledge of the chemical composition is always desirable, as is the case with all refractory clays. Further light may often be thrown upon the behavior of such clays by supplementing the ultimate analysis by the so-called rational or mineral analysis. This method, proposed by Forchhammer and Fresenius and amplified by Bischof, Richters, Seger, and others, depends upon the fact that clay substance and mica are soluble in boiling sulphuric acid, while quartz and feldspar are not. By treating the clay with hot concentrated sulphuric acid, diluting, filtering, washing with sodium carbonate, and finally with dilute acid solutions the clay substance plus mica may be removed from the clay. The residue composed of quartz and feldspar may then be partially analyzed by determining the silica and alumina or the alkalies and the content of the two mineral constitutents computed. This method is not scientifically exact and fails completely for the low-grade clays but, nevertheless, it is capable of giving useful results.

The presence of carbonaceous constituents in clays seems to contribute toward rendering them more plastic. It would seem, therefore, that a knowledge of the carbon content of such clays would be of service in explaining the behavior of these materials, since it is evident that the organic matter is an important element in developing the desirable quality of high plasticity.

5. DRYING SHRINKAGE AND DRYING BEHAVIOR

The strong plastic clays of the type under discussion show considerable contraction in volume upon drying. At the same time there is a distinct tendency on the part of some clays, such as the well-known Klingenberg material, to air check. Both of these items deserve attention. The difficulty due to air cracking is, of course, largely overcome in actual use by the employment of a large proportion of nonplastic material in the form of calcined clay, crushed potsherds (grog), and graphite. The drying shrinkage is determined by accurately calipering between shrinkage marks made on a bar of the clay in the plastic state and comparing the lengths in the wet and dried state. The shrinkage is usually expressed in per cent of the original or of the dry length. More accurate results are obtained by the use of the voluminometer, in which the volume contraction is determined. The measuring liquid commonly employed is kerosene. The measurement of the volume shrinkage is the only accurate method for determining this constant, since the linear contraction is not uniform in all directions but within certain limits is dependent upon the geometrical proportions of the test specimen. The shrinkage is also a function of the rate of drying, which is governed by the temperature (humidity) and the velocity of flow of the air around the piece being dried. As a rule the shrinkage is found to be smaller where the drying proceeds rapidly and larger where the process is taking place more slowly.

The behavior of a clay in drying can be estimated in a satisfactory way only by means of practical trials where the material is made up into larger pieces both with and without admixture of the nonplastic, inert constituents. Small laboratory trials usually are apt to deceive as to the real behavior of the clay.

6. EFFECT OF HEAT

Plastic fire clays may be roughly divided into two classes, namely, open and dense burning materials. The former when fired to high kiln temperatures, say, corresponding to pyrometric cones 14 to 16, retain their open structure, owing to the small amounts of fluxes, iron oxide, lime, magnesia, and the alkalies. The second type burns to a dense mass at these temperatures or below and may even show overburning or the formation of a vesicular, spongelike structure. Both types of clay are necessary. The first type is inherently more refractory and is able to withstand load conditions at furnace temperatures more satisfactorily. The second type is useful in closing up the pores of the material and producing a dense mass resistant to the corrosive action of slags and glasses. The ideal condition would be obtained by the use of a mixture of the two classes of clays and restricting the amount of the dense burning material to the minimum necessary to bring about the desired density. It is to be expected, of course, that there are to be found gradations between the two extremes, inasmuch as certain clays have some of the attributes of both classes.

The study of the rate of condensation or vitrification, a term not to be confused with the idea of glassiness, is usually followed by determining the decreasing absorption of water or porosity at a series of increasing temperatures. For this purpose specimens of the clay are made up in the shape of cubes or bars, which are fired in a kiln of sufficient size at a rate of temperature increase of about 20° C per hour. At intervals of 20° or 40° a specimen is withdrawn from the kiln and cooled slowly in hot sand or in a small furnace kept at a red heat. Upon determining the absorption or the porosity of the trials and correlating graphically these values with the temperature of withdrawal a diagram is obtained which is characteristic of the burning behavior of the clay. Decreasing porosity must, in the nature of the case, parallel the process of vitrification. The higher the content of fluxes the larger must be the quantity of the matter softening under the influence of the heat so that condensation or minimum porosity is reached at a comparatively low temperature. The open burning clays, on the other hand, show no striking drop in porosity and retain their porous structure at the temperatures involved. This behavior undoubtedly is due to their more refractory character, viz, the low content of fluxes. Such a diagram, first used by Purdy[8] for the study of clays, is extremely valuable in showing comprehensively what is taking place in a clay when being fired, and hence is a very valuable aid in classifying the clays.

It gives evidence not only concerning the vitrification temperature range of the materials but shows also when and to what extent the phenomenon of overburning takes place. By this is meant the formation of vesicular structure due to the evolution of gases. This is evidenced by the fact that during this stage the porosity again increases, since the clay becomes more or less spongelike in character. The usefulness of the clay is seriously lowered even during the incipient formation of this structure, as it is evidence that the clay has softened to a very great extent, and owing to the resumption of the greater porosity becomes more subject to the action of corroding slags or glasses. Fortunately in the presence of fine and coarser grained calcined clay of high refractoriness, grog, the formation of the vesicular structure is opposed by allowing the gases to escape more readily, by the solution of the fine-grained refractory clay with consequent stiffening, and by the mechanical effect of the skeleton of coarser grog particles. This condition is subject to regulation by the sizing of the grog, which makes necessary both the introduction of very fine particles and a series of coarser sizes. The adjustment of the sizes should be such that maximum density is produced in the dried state. It is specially important to keep in mind the function of the fine grog, a fact not as commonly realized as it should be.

A plastic clay which shows some formation of vesicular structure need, therefore, not be condemned on this evidence alone. If, however, it persists in bloating when admixed with grog, its use becomes decidedly questionable.

7. FUSION

It is well understood by this time that clays do not possess a definite melting point like minerals and metals. Softening takes

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[8] Illinois Geol. Survey, Bull. No. 9, p. 256.

place during a long-temperature interval. For purposes of comparison it is customary to determine that point at which small tetrahedra of clay soften to such an extent that the cones bend over completely, and we speak of this point, though wrongly, as the fusion or the melting point of the clay. In this connection it is important to note that time is an important factor, which is illustrated by the fact that this arbitrary degree of softening occurs at a lower temperature when the heating is continued for a longer time and vice versa.

For the purpose of establishing fairly well defined, fixed softening points which permit us to compare the refractoriness of the various clays, the well-known system of pyrometric cones was established by Seger. Pure clay, kaolinite, corresponding to the chemical formula $Al_2O_3.2\ SiO_2.2\ H_2O$, softens at cone No. 35, or approximately at the melting point of platinum, 1755° C. This point represents the highest type of refractory clay possible. The good fire clays, then, may range in refractoriness down to cone No. 28. The intervening numbers approximate the following temperatures: No. 34, 1740° C; No. 33, 1720°; No. 32, 1705°; No. 31, 1685°; No. 30, 1670°; No. 29, 1650°; No. 28, 1635°. These temperatures are only approximations, in the nature of the case, and it would be very desirable, indeed, if the use of temperatures in degrees were dispensed with entirely and the softening points indicated by means of the cone numbers. This would be a far more satisfactory and less confusing practice.

The ultimate softening temperature is apt to be a misleading criterion as regards the practical usefulness of a refractory, and in ceramic literature too much stress is placed upon this point. Thus, based upon the Seger kaolin-silica fusion curve siliceous clays are considered of an inferior grade compared with the high clay materials. As a matter of fact, clays high in silica and low in fluxes may show excellent refractory qualities in practical use and may stand up under severe conditions, as in gas benches and similar installations. The fact that the siliceous clays may fuse at a lower temperature, say at cone 30 or 31, is not of much practical significance. Such materials possess the important advantage of not softening throughout a considerable temperature range, as is the case with the clays approaching the composition of the pure clay substance and usually stand up at heats close to their ultimate softening point. The practice, for instance, of rating the siliceous New Jersey clays, which are low in fluxes, as second grade refractories must, therefore, be condemned.

The following pages deal with tests made upon typical plastic fire clays of established use in the industries.

III. DESCRIPTION OF WORK

1. MATERIALS STUDIED

As has been stated in the introduction of this paper, the object of this work is the study of typical European plastic fire clays which have been found to fulfill the requirements of industrial practice by many years, experience, so that the information might serve as a basis of comparison for similar American materials. Through the courtesy and cooperation of the Findlay Clay Pot Co., of Washington, Pa., a number of 500-pound samples were secured just prior to the outbreak of the European war, which were made available for this study.

The materials selected for this study were as follows:

A. A plastic clay from Gross Almerode, Germany, famous for its satisfactory behavior as a glass-pot material.

B. A very plastic clay from Klingenberg, Bavaria, generally used in the manufacture of graphite crucibles.

C. A plastic clay from the Kaschkau-Mehrener Tonwerke, near Meissen, Saxony, Germany.

D. A plastic pot clay from St. Loupe, France, which is extensively used in the French glass industry.

E. A plastic clay from the Westerwald district, Germany, obtained from Breitscheid, Dillkreis. This is a clay supposed to possess excellent qualities as a glass refractory.

Gross Almerode Clay.—This material is probably the best known of the plastic pot clays and was imported to the United States in considerable quantities. Ries[9] gives the following data concerning it. The chemical analyses of the clays from this region of Hesse-Nassau correspond to the following compositions:

	Crucible clay	Glass-pot clay
	Per cent	Per cent
Silica	47.50	72.05
Alumina	34.37	18.93
Ferric oxide	1.24	1.77
Lime	....	0.10
Magnesia	1.00	....
Potash	....	1.02
Loss on ignition	14.43	6.13

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[9] Mineral Resources of the United States, Report for the year 1901–1902.

"These clays are found in the tertiary formation and possess the property of burning dense at a comparatively low temperature. The pot clay requires 25.80 per cent of water for working, has an air shrinkage of 6 per cent and a tensile strength of 180 to 203 pounds per square inch. Its softening point corresponds to cone 27. It burns steel hard at cone 03 and assumes a very dense structure at cone 3."

Another authority[10] gives two chemical analyses of which No. 1 represents the bulk of the Gross Almerode deposit and No. 2 the best-known clay.

	No. 1	No. 2
	Per cent	Per cent
Silica	65.98	46.37
Alumina	23.37	35.62
Ferric oxide	2.32	2.25
Lime	.41	.88
Magnesia	.53	
Potash	.76	1.80
Loss on ignition	6.84	12.98

The clay being actually used in this country is evidently the more silicious material rather than that higher in clay substance.

Klingenberg Clay.—This material is especially favored for the manufacture of graphite crucibles and up to the present time has been used exclusively for this purpose by American makers. The best selection mentioned in the literature is said to approach closely the following composition:

	Per cent
Silica	54.06
Alumina	33.11
Ferric oxide	1.50
Lime	.49
Magnesia	.45
Potash and soda	1.37
Loss on ignition	9.12

The clay is mined near Klingenberg, Bavaria, and is one of the most plastic clays known. It appears to be quite high in organic matter. Unmixed with nonplastic matter it has a decided tendency to check and crack in drying. There are several grades of this clay on the market which differ in refractoriness.

Kaschkau-Mehren Clay.—This material is mined near Meissen, Saxony, and has the reputation of being a satisfactory plastic bond clay. It is the decomposition product of a porphyry.

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[10] Handbuch der gesammten Thonwaarenindustrie; Bruno Kerl, revised by E. Cramer and H. Hecht, p. 947.

Seger[11] gives as the composition of a typical plastic clay from this district the following figures:

	Per cent
Silica	63. 17
Alumina	25. 09
Ferric oxide	. 64
Lime	. 35
Magnesia	. 26
Potash	. 80
Chemical water	9. 70
Clay substance	67. 82
Quartz	30. 93
Feldspar	1. 25

Clay from St. Loupe.—In France refractory clays are found in the Paris basin, in the Département de la Marne, in the Bernon Mountains, and near Bollene or Noyeres. Attention might be called also to the excellent fire clays found near the boundary line between France and Belgium, such as the famous clay from Andenne, near Namur, and the pot clays from Navelin, Strud-Maiseroul, Ohey-Matagne, Tahier, and Soree. The most plastic and refractory material is that from Strud-Maiseroul. An analysis of the Ardennes clay is given by Ries[12] as follows:

	Per cent
Silica	49. 64
Alumina	34. 78
Lime	. 68
Magnesia	. 41
Ferric oxide	1. 80
Alkalies	. 71
Loss on ignition	12. 10
Total	100. 12

Westerwald Clay.—This clay comes from one of the extensive deposits in Hesse-Nassau, associated with lignite beds, and which extend into the valley of the Rhine. Well-known deposits are found at Hoehr, Grenzhausen, Ebernhahn, Wirzes, Giroden, Limburg, Vallendar, Breitscheid, and many other localities. The sample available was from Breitscheid (Dillkreis). The Westerwald clays show a wide range of compositions and vary from the siliceous stoneware clays of Hoehr to the purer clays of Vallendar, in the Coblentz district, on the east side of the Rhine Valley.

2. TESTS MADE

With reference to the properties of the clays in the raw state, both plastic and dry, determinations were made of the amount of

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[11] Gesammelte Schriften, p. 344.

[12] U. S. Geol. Survey, Mineral Resources, 1901.

water required for normal consistency, the relation between different water contents of the same clay and the drying shrinkages, of the Atterberg plasticity factor, of the fineness, the tensile strength in the plastic state, the time of disintegration in water, the tensile and transverse strength in the dried state, both without and with admixture of nonplastic, and an estimate of the drying behavior.

As regards the properties of the materials upon firing, the absorption and the porosity were determined for each clay when heated to a series of temperatures as well as the apparent specific gravity and the final softening temperature.

3. WATER CONTENT AND DRYING SHRINKAGE

The clays were made up with percentages of water, varying from the amount required to cause minimum plasticity or working quality to that in which the materials had become soft and had reached the upper limit. The linear drying shrinkage was determined in each case. This work included, of course, the determination of the water content at normal consistency and the drying shrinkage both at room temperature and in a constant temperature oven at 65° C. The water content in each case was determined by drying at 110° C in an electrically heated oven.

The Atterberg plasticity number was obtained as described by Kinnison.

The estimation of fineness consisted in determining the percentage of clay removed in the elutriation test by a water current of 0.18 mm per second. The Schoene funnel was employed for this purpose. In order to secure satisfactory results it was necessary to deflocculate the clays either by using 0.1 per cent of caustic soda in terms of the dry weight of the clay and slaking the 5-gram sample with 100 cc of distilled water or to use an alkaline solution throughout the washing process, possessing a strength of 0.01 per cent caustic soda. A fine screen was inserted in the lower part of the funnel, as recommended by Seger. The temperature of the water was kept very close to 21.5° C. The amount of clay removed by washing was determined by weighing the residue left in the funnel.

The time of disintegration in water was determined by making seven-eighths-inch cubes of a 1 : 1 mixture of the clay and potter's flint thoroughly mixed together, drying the cubes at 110° C and then immersing them in water at room temperature. During the immersion the cubes were placed on coarse mesh wire baskets suspended in the liquid.

4. MECHANICAL STRENGTH OF THE CLAYS

The tensile strength of the clay specimens, possessing the shape of the standard cement briquette, was readily determined by using one-half of the brass mold as the top clip and as the lower one a clip made from plaster of Paris, which was shellacked. The load was gradually applied by causing a small stream of water to flow into a light pail. The stream was interrupted automatically as the specimen broke. Failure in each case was preceded by rupture cracks and elongation.

The tensile strength in the dry state was determined as usual, employing specimens of the form of cement briquettes. The bars for the transverse test were pressed in brass molds and were of the dimensions 6½ by 1 by 1 inch in the green state. All specimens subjected to these tests were first dried at room temperature until shrinkage had ceased, then to constant weight at 75° C, and the drying completed at 110° C, a practice recommended by C. H. Kerr.[13]

Since plastic clays are subject to strains in drying which may lead to the formation of visible or invisible cracks, and hence to abnormal results in the tests, such determinations made upon unmixed clays must be looked upon with caution. Even very strong clays may give poor results because of drying defects. It would be desirable if a uniform practice of using a 1:1 mixture of the clay and a standard sand could be adopted, since this procedure would do away with the difficulty mentioned. In the present work, in addition to the tests of the unmixed clays, mixtures of the clays with grog, produced by calcining a high-grade flint clay, in the proportion of 1:1, by weight, were employed. This grog was obtained through the courtesy of the Harbison-Walker Refractories Co., Pittsburgh, and showed the following sieve analysis:

	Per cent
Grains between 10 and 20 mesh sieve	0.1
Grains between 20 and 30 mesh sieve	13.9
Grains between 30 and 40 mesh sieve	19.9
Grains between 40 and 60 mesh sieve	16.2
Grains between 60 and 80 mesh sieve	5.6
Grains between 80 and 100 mesh sieve	5.5
Grains between 100 and 120 mesh sieve	8.1
Grains between 120 and 150 mesh sieve	2.5
Through between 150-mesh sieve	26.6

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[13] Trans. Am. Ceramic Soc., 15, p. 345.

A sufficiently large amount of this grog was available to serve for all of the tests. It is evident, of course, that calcined clay of another combination of sizings would give somewhat different results.

5. DRYING BEHAVIOR

The drying qualities of the clays were estimated by measuring the linear shrinkage and by determining the length of time elapsing before shrinkage ceased, the drying being conducted in an electrically heated oven maintained at a constant temperature of 65° C. Multiplication of the percentage of linear shrinkage by the time in hours elapsing until complete shrinkage has taken place, results in a factor indicative of the resistance of the clay to drying and the value, hence expresses the difficulty experienced in taking it through this process.

6. BEHAVIOR DURING VITRIFICATION AND FUSION

The burning behavior of the clays was determined by making up a series of 2-inch cubes of each material and firing them in a large gas-fired test kiln up to the maximum temperature, close to 1400° C, at a rate corresponding to a temperature increase of 20° C per hour beyond about 1000° C. Care was taken to allow sufficient time for the proper oxidation of the clays. The kiln temperature was measured by means of platinum-platinum-rhodium thermocouples and Siemens-Halske galvanometers. Beginning with 1125° C a specimen was withdrawn, at intervals of 25° C, from each set and cooled slowly in a heated pot furnace. The porosity of the cold pieces was then determined by obtaining the weight of the dry pieces, that of the completely saturated, and finally of the saturated piece suspended in water. The absorption of the specimens was obtained by boiling till constant in weight. The porosity was then computed from the relation: $100\frac{(W-D)}{(W-S)}$, where W = weight of the saturated briquette, D = weight of dry briquette, and S = weight of specimen, suspended in water at room temperature. This porosity value is equivalent to the absorption, in terms of the weight of the dry piece, multiplied by its apparent specific gravity. From the above data the apparent specific gravity was also readily calculated.

In addition the softening point of each clay was determined in an electric muffle furnace using granulated carbon as a resistor.[14]

The clays under examination were also analyzed as to their ultimate composition.

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[14] Tech. Paper No. 7, this Bureau.

IV. RESULTS OF TESTS

1. PROPERTIES OF THE CLAYS IN THE RAW STATE

The results bearing on this part of the work are compiled in Tables 3 and 4. In Table 3 the relation between the varying water content of the clays and their linear drying shrinkage is given. These results are also shown graphically in Fig. 1. It is evident on inspection of these data that clay A (Gross Almerode clay) has a much shorter range of water content than any of the other clays, showing a difference between maximum and minimum of 26.14 per cent, while the others range between 48.25 and 59.62 per cent. Similar observations obtain in connection with minimum and maximum drying shrinkage. The water content at normal plasticity, as is to be expected, is lowest in clay A and highest for the Kaschkau clay. Clays B and D are closely related, D representing a more desirable form of the curve. Clays C and E indicate an excessively water-laden structure. The short range of clay A and its low drying shrinkage show at once its granular physical state. The above results are not contradicted by the Atterberg plasticity factor, though this value is not as discriminating since it is practically the same for the last three materials.

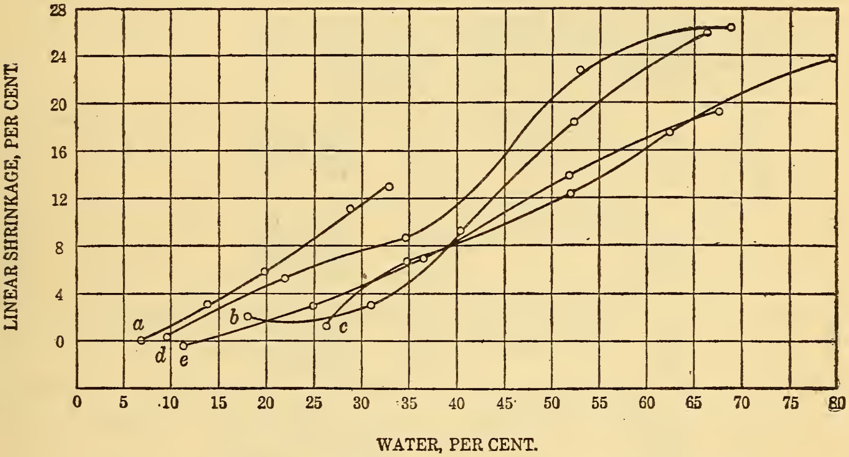

FIG. 1.—*Relation between water content and linear drying shrinkage*

TABLE 3

Clay	Minimum water content with which clay can be worked		Water content between minimum and normal		Normal consistency		Water content between maximum and normal		Maximum water content with which clay can be worked		Difference between maximum and minimum water content	Difference between maximum and minimum shrinkage
	Per cent water	Per cent linear drying shrinkage	Per cent water	Per cent linear drying shrinkage	Per cent water	Per cent linear drying shrinkage	Per cent water	Per cent linear drying shrinkage	Per cent water	Per cent linear drying shrinkage		
A	6.61	0.21	13.80	3.17	19.64	5.91	28.60	11.01	32.75	13.00	26.14	12.79
B	17.95	2.02	31.00	3.06	40.12	9.41	52.25	18.33	66.20	24.92	48.25	22.90
C	26.12	1.62	33.28	6.18	42.72	8.63	62.10	17.66	79.83	23.75	53.71	22.13
D	9.33	.39	21.98	5.32	34.95	8.87	52.90	22.83	68.95	26.25	59.62	25.86
E	10.82	.07	24.90	3.14	36.50	5.92	51.80	13.96	67.50	19.58	56.68	19.51

TABLE 4

Clay	Source	Water of plasticity for normal consistency per cent of dry weight	Linear drying shrinkage room temperature, per cent of dry length	Atterberg plasticity number	Fineness, amount of clay removed by water current of 0.18 mm per second, per cent by weight	Tensile strength in plastic state, pounds per square inch	Time of disintegration of dried clay in water, minutes	Tensile strength of dried clay, pounds per square inch	Modulus of rupture of dried clay, pounds per square inch	Tensile strength of dried clay, with 50 per cent grog, pounds per square inch	Modulus of rupture of dried clay, with 50 per cent grog, pounds per square inch	Drying factor	Drying behavior of clay
A	Gross Almerode	19.64	5.91	40.4	61.2	2.81	50.0	227.50	563.0	160.6	399.8	29.5	Good.
B	Klingenberg	40.12	9.41	63.3	54.6	4.05	(a)	62.9	301.0	177.5	538.0	75.3	Cracks.
C	Kaschkau	42.72	8.63	108.1	61.3	3.40	39.0	103.6	297.5	113.0	270.6	60.3	Do.
D	St. Loupe	34.95	8.87	105.7	86.1	4.42	(a)	59.3	475.0	226.1	431.3	62.1	Inclined to crack.
E	Breitscheid	36.50	5.92	102.6	90.8	2.35	16.3	91.5	258.0	90.6	195.8	35.5	Good.

[a] Longer than 120 minutes.

An interesting relation brought out by the closer study of the total water content and the drying shrinkage is that between the shrinkage volume or the volume of the shrinkage water and the volume of the pore water. This computation may be made more comparable by expressing them in terms of the true volume of clay, namely, its weight divided by the specific gravity which may be taken to be 2.60 for this type of clay.[15] These figures have been collected in Table 5.

TABLE 5

Percentages of Shrinkage and Pore Water in Clays

Clay	Per cent shrinkage water, in terms of true clay volume	Per cent pore water, in terms of true clay volume	Ratio of per cent shrinkage to per cent pore water	Per cent total water, in terms of true clay volume	Per cent shrinkage water, in terms of total water
A	23.9	27.1	1:1.13	51.0	46.4
B	48.3	56.0	1:1.13	104.3	46.3
C	46.5	64.5	1:1.38	111.0	41.9
D	43.4	47.5	1:1.09	90.9	47.7
E	30.6	64.3	1:2.10	94.9	32.2

It appears from these values that the relation between the shrinkage and pore water and the shrinkage and total water volumes are particularly significant. It seems that the lower the first ratio and the higher the percentage of shrinkage water in terms of the total water volume the stronger, mechanically, is the clay. Thus, clays A, B, and D are strong, as is shown by the modulus of rupture tests of the clay-grog mixtures, and possess low shrinkage-pore water ratios, while C and E are much weaker and show considerably higher ratios. Clay E having much the highest ratio and the lowest percentage content of shrinkage water is also the weakest clay of the series. This is in agreement with theoretical considerations since a high content of pore water points toward an excessive degree of dispersion. It would seem desirable, therefore, to make use of those relations in the study of clays as their practical importance is manifest. It is to be regretted that those relations have received no attention in previous investigations. Arranging the clays, therefore, with reference to their plasticity, strength, and bonding power they would be classed in the following order: Klingenberg, St. Loupe, Gross Almerode, Kaschkau, and Breitscheid clay. The drying shrinkage, per se,

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[15] Bureau of Standards, Tech. Paper No. 1, p. 45.

is a criterion of plasticity and the values obtained point to the clays B, C, and D as being the most plastic materials. Since the drying shrinkage is a variable, dependent on the drying temperature, water content, and general rate of evaporation, it is a factor not suitable for close differentiation except when determined under well-defined conditions.

The fineness of the clays as estimated by the amount elutriated with minimum current velocity does not assist in differentiating the materials with any degree of precision. A clay showing the greatest fineness of grain or dispersion is not necessarily the most plastic, and in fact there seems to be a definite limit which, however, has not yet been established. This condition has been realized by Ashley [16] who introduced fineness, measured by the surface factor, in his formula as being a factor inversely proportional to plasticity. Great fineness in general opposes what is usually considered normal, or working plasticity, inasmuch as it brings about a condition which might be termed "excessive plasticity." Such a state may be recognized also by the high value of the ratio pore water: shrinkage water. It is entirely possible that our means of estimating fineness by elutriation, etc., may be entirely inadequate for the purpose. It is possible to imagine a large portion of comparatively coarse granular material cemented together by a small amount of a glue-like emulsoid. The percentage of weight removed in the elutriation would be small and hence the information would tend to be misleading. The ordinary methods of mechanical analysis fail to give us a true estimate of the fineness of the dispersed matter.

The tensile strength of the clays in the plastic state showed a decided superiority on the part of clays B and D. Apparently the clays A and E are so much weaker that they seem to show no relationship to the other materials.

Curiously, similar evidence is furnished by the disintegration test in water. Here, again, clays B and D resist the slaking action for a long time. Clay E breaks down quickly, while A and C show approximately the same behavior. This again points out the strongly plastic nature of B and D which is in striking contrast to that of E. It would seem that the last-named clay is more of a kaolinic nature. The slaking test is valuable in enabling us to estimate quickly the nature of a plastic bond clay. A material breaking down rapidly under the conditions of the test gives little promise of being useful in this direction.

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[16] U. S. Geol. Survey, Bull. No. 388.

Considering the transverse strength of the dried clay-grog mixtures as the best criterion of the mechanical strength, the clays range in the order of B, D, A, C, and E. The superiority of B and D is again evident. At the same time the strength of the Gross Almerode clay reaches a remarkably high value, considering its low content of clay substance proper. Its actual strength causes it to rank among the very best clays, and if we consider its easy drying qualities and slight tendency to laminate, it is readily understood why it has proven so useful in the glass industry. Both C and E appear at a considerable disadvantage from this standpoint, clay E being especially weak.

Inspection of the drying factors (Table 4) indicates that B is the most difficult and A the most easily drying material, followed closely by E. The explanation of the excellent drying qualities of A lies, of course, in the high content of fine quartz sand, while that for E must be ascribed to the water-laden structure of the clay which allows ample capillary flow and hence comparatively rapid evaporation of the water, just as some fine-grained kaolins like those from North Carolina, with a high pore water content, dry with the greatest ease. This is similar to the condition prevailing in the so-called slop-molded bricks, which dry more easily than when the clay is formed with less water. It should be expected, however, that a limit must be reached in this direction when the total water content becomes too high and hence the capillary system too fine, so that drying again becomes difficult.

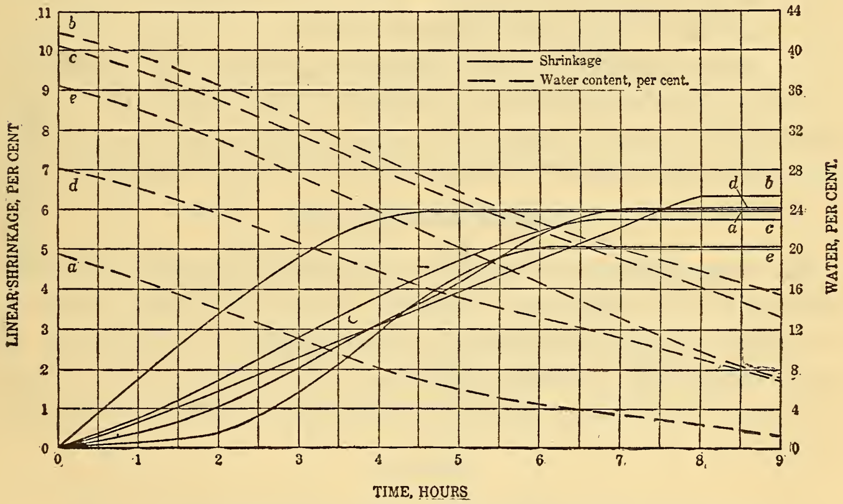

FIG. 2.—*Diagram showing rate of water evaporation and rate of shrinkage*

The drying behavior of these clays is illustrated also in Fig. 2, showing both the linear shrinkage and the percentage water content upon drying the clays at a constant temperature of 65° C. It is at once seen that the shrinkage is completed earliest with A and last with B. By reading the water content of each clay from the point where shrinkage has ceased, upon the percentage water curve, the approximate amount of residual or pore water is obtained.

From a general review of the physical properties of these bonding clays it would seem that the clays B and D are the most valuable materials where a dense initial structure and high mechanical strength are necessary. Hence they would be most serviceable in the manufacture of graphite crucibles for which the clays A, C, and E would not be so desirable. For glass refractories the excellent qualities of the Gross Almerode clays are evident. The inferior drying qualities of the Klingenberg clay would render it unsatisfactory for such heavy products as glass pots, etc. The latter clay could be improved in this respect even for graphite refractories by admixture with a clay of the Gross Almerode type.

2. BURNING BEHAVIOR

The most satisfactory study of the burning behavior of clays is afforded by the temperature-porosity diagram, in which the drop in porosity which is equivalent to the progress of vitrification is shown graphically. Such a diagram for the clays under discussion is presented in Fig. 3, and the corresponding values are compiled in Table 6.

TABLE 6

Clay	Percentage porosity of specimens when fired to the temperatures, °C—											Per cent burning shrinkage at maximum temperature	Softening point of clay, standard cones
	1125	1150	1175	1200	1225	1250	1275	1300	1325	1350	1375		
A.......	19.95	18.13	18.00	16.68	15.83	15.10	12.53	12.93	11.55	10.80	8.00	3.34	28+
B.......	4.40	3.70	3.75	4.10	4.09	4.41	3.94	4.40	....	3.72	4.70	8.01	30+
C.......	14.50	10.90	8.05	3.27	3.25	3.04	3.06	3.96	3.37	3.17	3.12	5.55	32+
D.......	12.50	8.85	6.77	6.83	6.02	3.44	....	3.40	3.21	3.66	3.42	8.05	32
E.......	8.25	6.12	5.20	1.74	2.25	2.71	3.33	3.21	3.60	4.02	7.02	5.6	32

The porosity determinations were not begun until a temperature of 1125° C was reached. The initial porosities of the several clays at this point afford considerable interest. It is noted at once that clay A, as is to be expected, remains most porous at this temperature while clay B shows the greatest contraction and has reached a state of advanced vitrification and density, the other clays arranging themselves within these extremes. Between this and the maximum temperature, 1375° C, clay A becomes slowly denser corresponding to a leisurely progression of vitrification while clay B, in spite of its advanced vitrification, retains this condition up to 1350° C when it begins to become more porous owing to the formation of a vesicular or spongy structure due to overburning. This is truly a remarkable behavior for a clay of this type. While in the case of B the large porosity drop from the most porous condition has already taken place below 1125° C it still proceeds in all of the other clays, being slowest in the case of A. Materials C and E reach their minimum porosity or maximum degree of vitrification at 1200° C, although there is quite a difference between

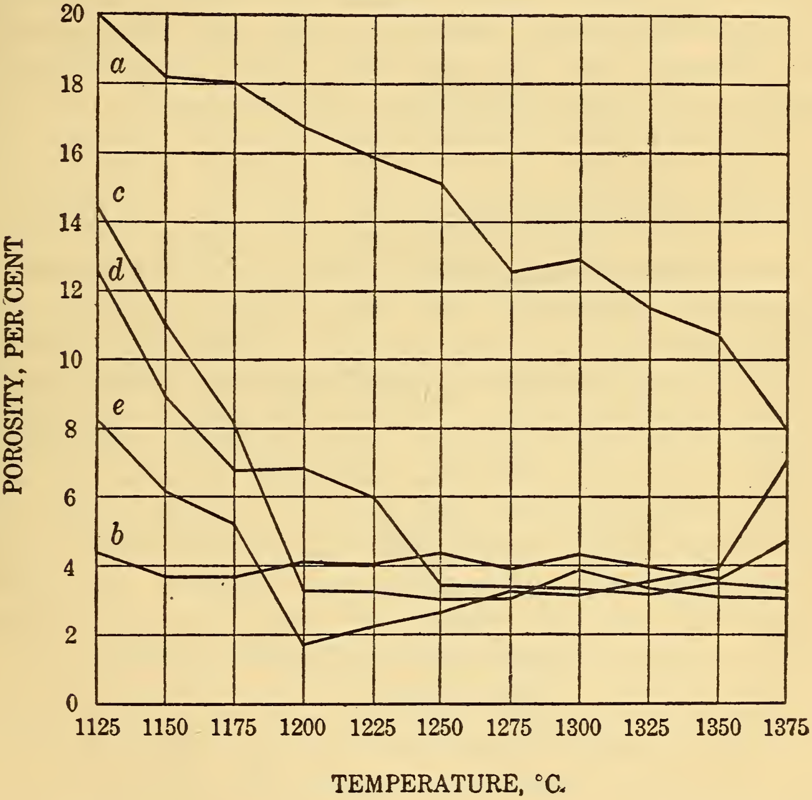

Fig. 3.—*Relation between burning temperature and porosity*

the two clays. Clay C vitrifies comparatively rapidly between 1125° and 1200° to a porosity of 3.27 per cent, which causes it to be denser than the Klingenberg clay, and retains this condition quite consistently up to and beyond 1375° without any evidence of vesicular structure. Its burning behavior is therefore eminently satisfactory, and the only advantage shown by the Klingenberg clay is the low vitrification temperature, a consideration of importance in graphite crucibles used for brass melting but a minor consideration for steel. Material E, on the other hand, becomes very dense at 1200° (1.74 per cent porosity), but immediately begins to show increased porosity, due to overburning. Clay D shows a more gradual vitrification than the other clays with the exception, of course, of A and reaches a density somewhat lower than that of B at 1250° (3.44 per cent porosity). It retains this condition up to and evidently beyond 1375°. It shows, therefore, a most excellent burning behavior, and would seem to be better adapted for graphite crucibles used in steel making than the Klingenberg clay. As far as graphite crucibles are concerned clay A is out of the question, though it appears to be most satisfactory as a glass refractory. Clay E, likewise, is to be eliminated because of its ready tendency to become vesicular. This leaves, then, the clays B, C, and D for consideration. For crucibles used at lower temperatures the Klingenberg clay is without doubt the peer of these, since it becomes dense at a low temperature (1125° C) and thus protects the graphite from oxidation. For higher temperature work, say, above 1325° C and D have the better of it. Of these D shows the more refractory behavior and C, having evidently a higher content of fluxes, matures at a lower temperature. The slower vitrification of D may be of advantage in some cases where temperatures above 1250° are involved or it may be a disadvantage at lower temperatures, as in the case of graphite crucibles, where it may leave the structure open too long and hence cause oxidation of the carbon. This French clay, however, appears to be a magnificent material for glass pots and other refractories of this type. Although not quite as excellent the Kaschkau clay likewise appears to be promising for the same purpose from the standpoint of heat behavior. A mixture of either C or D with A would result in a most satisfactory combination for glass refractories, especially since the ultimate refractoriness would thus be improved.

With respect to burning shrinkage at 1375° C the clays B and D, on the one hand, and C and E, on the other, agree substantially. The low burning shrinkage of clay A is to be expected from a knowledge of its properties.

The softening temperatures determined indicate that clays A and B are the least refractory materials, a point not of primary importance as far as graphite crucibles are concerned, but more vital with reference to glass refractories. Its low softening temperature is undoubtedly a drawback of the Gross Almerode clay and the admixture of a more refractory material like the fire clays of the St. Louis, Mo., district would be very desirable. Clays C, D, and E are about of the same refractoriness, corresponding to cone No. 32, which is typical of high-grade fire clays and exceeds that of the ordinary bond clays employed in the manufacture of fire bricks.

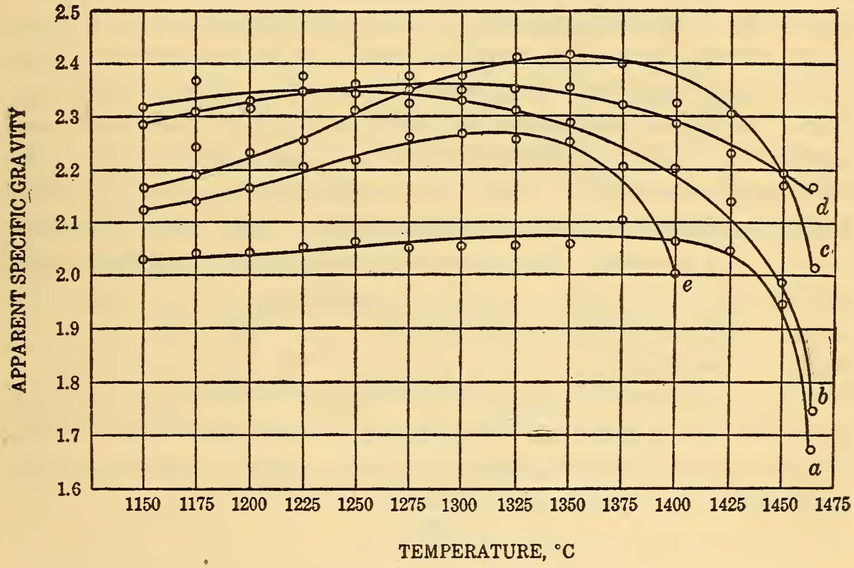

Fig. 4.—*Relation between burning temperature and apparent specific gravity*

The results of the apparent specific-gravity determinations upon the clay specimens fired to different temperatures are shown in Fig. 4. Two of the materials, C and E, show rather unusual specific-gravity changes, inasmuch as the density increases markedly up to a certain temperature, 1350° and 1325°, respectively, and then drops as vitrification proceeds. The other clays do not exhibit such a behavior, though material A undergoes a slight increase in density previous to the drop associated with vitrification. The most marked lowering of the apparent specific gravity is observed in the case of the least refractory materials, A and B, a fact in agreement with the observation that the true volume of clays increases, coincident with vitrification, irrespective of the external contraction suffered by a molded piece. From the data of the specific gravity values clay D is the most refractory material, apparently lowest in fluxes, and the remaining clays, according to their refractoriness, would arrange themselves in the order C, E, B, and A.

3. CHEMICAL COMPOSITION

Inspection of the chemical analyses of these clays (Table 7) throws no light upon the physical characteristics of the materials. Certain facts, however, are of interest, such as the ratio of silica to alumina and the contents of ferric oxide, lime, magnesia, potash, and soda. The silicious nature of the Gross Almerode clay at once becomes prominent with its silica content of 73.08 per cent. None of the clays approach the composition of kaolinite (47 per cent silica and 39 per cent alumina) closely. The titanium oxide content is high in samples A and D. The percentage of ferric oxide does not exceed 1.5 per cent. It is noted, also, that clay A contains the smallest amounts of fluxes (Fe_2O_3, CaO, MgO, K_2O, and Na_2O), 1.92 per cent, this value being 4.63 for B, 2.54 for C, 2.19 for D, and 4.62 for E. In all the materials but A the clay substance varies between 76 and 80 per cent. Clay E is highest in feldspar and lowest in quartz content. The small percentage of feldspar in clay D is remarkable. The low vitrification temperature of B is explained by the high content of total fluxes. Probably a flux content of about 3 per cent would be somewhat more desirable.

TABLE 7

Clay	Silica	Alumina	Titanium oxide	Ferric oxide	Lime	Magnesia	Potash	Soda	Loss on ignition	Total	Clay substance, calculated	Quartz, calculated	Feldspathic matter, calculated
	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
A.....	73.08	15.75	2.10	0.62	0.54	0.33	0.27	0.16	7.11	99.96	44.28	53.03	2.69
B.....	50.76	29.26	1.61	1.51	1.08	.73	.85	.19	14.24	100.23	80.64	12.86	6.50
C.....	54.13	29.06	1.57	.84	.75	.31	.32	.32	12.63	99.93	78.46	17.54	4.00
D.....	55.40	27.07	2.40	1.02	1.04	.42	.06	.05	12.47	99.93	76.69	22.63	.68
E.....	52.11	30.99	1.10	1.59	1.26	.10	1.25	.42	11.20	100.02	78.37	11.53	10.10

4. COMPARISON OF CLAYS

It should be clearly understood that each particular use of refactories emphasizes certain specific requirements which may be best met by a certain material. This may be illustrated by a concrete illustration. The bond clay serving best for graphite crucibles to be used for brass melting evidently is one which becomes dense at a comparatively low temperature, thus excluding the oxygen of the air from the carbon grains by enveloping them with a protective layer of clay.

Summarizing all the data obtained in this work, it is evident that the Klingenberg material serves this purpose best up to a temperature of about 1350° C, and probably somewhat higher, since it seems that the admixture of graphite tends to increase the refractoriness of the mass. Although this temperature limit would include also that required for melting steel, it is very probable that a material like the St. Loupe clay would be superior for this purpose. For glass refractories, like pots and tank blocks, the Gross Almerode type of material seems best adapted as far as its physical qualities are concerned; but, as has been stated before, even this clay could be improved by the addition of a more refractory plastic bond clay, such as the French clay. The latter material would be well suited as a bond clay for glass pots if it could be dried somewhat more easily. It represents probably the best all-around plastic fire clay of this series.

5. REPLACEMENT OF FOREIGN BY DOMESTIC CLAYS

The question of replacing the plastic clays, imported from Europe in considerable quantities up to the outbreak of the European war, has been of importance to the industries concerned. The materials which are chiefly concerned are the Gross Almerode clay for the glass and the Klingenberg clay for the graphite crucible and allied industries. The physical qualities of these materials have been set forth in detail in the preceding report.

Some of the users of such materials have sought to replace these clays by individual American clays. There is no reason to believe that such clays can not be found in the United States; in fact, materials have been tested in this laboratory which approach the foreign clays in quality. It would be far better, however, to depend upon a mixture of two or more clays, representing both clays of the open and more refractory and of the dense and vitrifying variety to secure the desired condition. Since such clays as those from the St. Louis, Mo., district have been used for years with good success in glass-pot mixtures, in conjunction with the European clays, it would not be difficult to supplement their qualities by means of materials vitrifying at lower temperatures and not subject to overburning within a considerable temperature range. Such clays, it is true, are not common, but may be found among the ball clays or semiball clays of Tennessee and Kentucky and in some of the plastic No. 2 fire clays, as those from Pennsylvania and Ohio. It is important to realize that an open burning clay of the Gross Almerode type, whether it be like the plastic clays from Missouri or New Jersey or the silicous clays from Arkansas, should be blended with one or more clays of the opposite type and not with materials of the same class, a mistake which is sometimes made. Likewise, it should be realized that a bond clay suitable for glass work is not necessarily adapted for use in graphite crucibles where greater density of structure at lower temperatures is essential, a fact strikingly illustrated in the difference between the properties of the Gross Almerode and Klingenberg clays. By adjusting the proportions of the two kinds of clay and by thorough mechanical blending through fine grinding, the desired quality can be obtained as well as maintained with results which should be superior to those which have been had with the single imported clays. The claim that no American clays are available which answer the purposes of the industries involved is fallacious, a fact supported by actual foundry results communicated to the writers. Open-burning plastic clays of good refractoriness are found in Alabama, Colorado, Georgia, Arkansas, Illinois (southern part), Kentucky, Missouri, New Jersey, Ohio (southern part), and Tennessee. In the same States, and frequently close to other deposits, dense burning clays are also found, to which must be added materials of this class found in Maryland. There is no lack of materials, and it is a question only of selection.

V. SUMMARY

Based on the results of the work described in the preceding pages, the writers venture to suggest certain tentative specifications which might be of service in selecting plastic bond clays. The tentative character of these suggestions is emphasized and it is realized that modifications and amplifications will be necessary.

Plastic bond clays should possess a considerable water-shrinkage range, one of about 40 per cent between the minimum and the maximum water contents, permitting of molding of the clay. In the case of silicious clays, allowance should be made for the content of nonplastic constituents and the permissible range reduced to 20 per cent, provided the materials fulfill all other essential requirements. The Atterberg plasticity number should not be lower than 50 nor higher than 110. The ratio of the percentage of the shrinkage to the per cent of pore water should not be greater than 1:1.2. The total water content, for normal consistency, expressed in terms of the dry weight, should be between 30 and 45 per cent. When intimately mixed with 50 per cent of potters flint (by weight) the time of complete disintegration in water of a seven-eighth inch cube in the dried state, made of the mixture, should not be less than 50 minutes, the water being at room temperature. The tensile strength of the clay in the plastic state should be close to 4 pounds per square inch. The linear drying shrinkage should not be less than 6.5 and more than 10 per cent of the dry length, the drying to be done at room temperature.

When made up with 50 per cent, by weight, of hard burned grog, which passes the 20-mesh sieve and shows residues of 34 per cent on the 40 mesh, 27 per cent between 40 and 100 mesh, 12 per cent between 100 and 150 mesh, and of which 27 per cent passes through 150 mesh, suitable dried test specimens should show the following minimum strengths: Tensile strength, 150 pounds per square inch; modulus of rupture, 350 pounds per square inch. The drying should be so conducted that the specimens are kept at room temperature until shrinkage has ceased, when they are to be heated to 75 and 110° C, respectively, and to constant weight in each case.

Dried specimens of the clay should be fired in a suitable kiln at a rate, corresponding to a temperature increase of approximately 20° C per hour, beginning at 1000° C and withdrawn from the kiln at intervals of 20 or 25° C. Absorption and porosity determinations should be made upon all pieces. The clays should show a porosity of not more than 10 per cent at 1150° C, at 1250° approximately 5 per cent, and should then maintain practically constant porosity up to 1350° in the case of materials intended for graphite crucibles used in brass melting and 1400° for crucibles employed for steel. For glass refractories, minimum porosity need not occur at as low a temperature, nor is it necessary that the clay burn to as dense a structure. In this instance the porosity at 1350° should not be greater than 10 per cent and should show no increase due to vesicular structure. The linear burning shrinkage may vary, for the unmixed clay, from 5 to 8 per cent, in terms of the dry length, and should not exceed the higher limit. The softening temperature of the plastic clays should not be below that corresponding to cone No. 30 and for glass refractories it would be desirable to have it higher.

The percentage content of total fluxes, Fe_2O_3, CaO, MgO, K_2O, and Na_2O may approach 5 per cent for crucible clays but should not exceed 4 per cent for clays used in glass refractories.

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