

## CLAY TECHNOLOGY IN CERAMICS

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### ABSTRACT

Clays are used in the ceramics industries largely because of their contribution to the moulding and drying properties of the wares being produced; many clays, such as the flint clays, are used because of favorable behavior during firing or because they produce favorable properties in fired ware.

To assure the most effective use of a clay, the ceramic technologist must meet problems of purification, aging, bacterial action, and the improvement of the working properties of clays and bodies through additions of non-plastic materials or chemicals. He deals with flocculation and deflocculation, thixotropy, and related phenomena in casting slips. Control of drying behavior is important. Finally, the ceramist is concerned with the influence of the clay content of ceramic bodies on their behavior during firing.

*Introduction.* Ceramics is defined (Wilson 1927; Ries 1927; Committee on Definition of the Term "Ceramics," 1920; Norton, 1952) as the arts and sciences of making products and articles (a) chiefly or entirely from "earthy" raw materials, that is, from the so-called non-metallics excepting fuels and ores of metals; and (b) with a high temperature treatment involved, either in manufacturing or in service. The technology of clays in the field of ceramics, therefore, includes consideration of both the room-temperature properties and the behavior at elevated temperatures.

When clays are used in ceramics, one of several functions is generally served. Most clays, alone or in mixtures, are used chiefly for their contribution to the working properties, drying strength, and dry strength, of the ceramic masses which they comprise or to which they have been added. Some clays, however, are used more because they offer an inexpensive body constituent or filler of the desired chemical composition, already subdivided by nature to a convenient grain size. For example, china clay probably serves as much or more as a filler than as a plasticizer in some dust-pressed wall-tile. Other applications of clays for their refractory or fired properties include the use of raw or calcined flint clay as a grog in refractories or as an investment material in precision casting.

Throughout the ages, clays have been recognized as being highly individualistic. It must have made a lot of difference to the ancient potter whether his clay was satisfactory or not; the average ceramic engineer of today still buys clays by name in order to obtain the particular properties necessary for his purposes. Because of variations from shipment to shipment, even this practice causes undesirable variations of operations within the plant.

It is surprising that an industry which has been so closely associated with the use of clays for so many centuries should have contributed relatively so little to the understanding of the fundamental nature of clays. Although the ceramic literature contains numerous reports of empirical investigations and of practical applications, much of the basic theory has come from the fields of colloid chemistry, mineralogy, physical chemistry, soil science, and petroleum production. It probably

is to be expected, however, because of the educational background and training of most of the researchers in this field, that much of the scientific work done on the ceramic clays would be carried out by colloid chemists or physical chemists. The ceramic technologist has not meant any disrespect to the mineralogist in doing this, but it has served his purposes better as far as plant control is concerned.

One of the difficulties facing the layman in attempting to obtain a systematic picture of clay technology in ceramics is that such a wide variety of shaping methods is employed, ranging from dust pressing, on the low moisture side, through stiff-mud extrusion, hot pressing, soft-mud moulding and jiggering, to slip casting at the higher liquid extreme. Individual companies use various clays, in varying amounts, and in different conditions of flocculation and deflocculation, for a variety of purposes. The same clay, therefore, which is considered highly satisfactory for one product may be entirely unsuited for another; there apparently are almost no entirely good or bad ceramic clays.

This condition perhaps explains much of the confusion and contradiction found in the reports on investigations of clay problems, particularly those of earlier years; it was not enough that varying amounts of the same reagent could affect a natural clay in opposite directions; two researchers in interpreting the same results were all too likely to have opposite criteria as to whether the reported changes in physical properties brought about by the experimental conditions were beneficial or detrimental.

Ceramic classification of clays is undergoing a revision. Clays used to be known according to the product best made from them: brick clays, terra cotta clays, sewer pipe clays, refractory bond clays, and the finer ball and china clays. The newer classification will be on the basis of mineral constitution. A re-examination of many clay and shale deposits is now underway, to see if kaolinite actually is the predominating clay mineral as had been previously reported. The clay technologist now definitely recognizes the need for better identification of the clay minerals in his clays, whether mined at the plant or purchased.

*Properties of Unfired Ceramic Clays.* It is well known that when clay is mixed with sufficient water, a mass is formed which exhibits typical plastic flow, that is, has a yield stress and a measureable mobility. The ceramist, however, is vitally interested also in still a third factor, the extensibility; that is, how far the clay can be deformed before tending to rupture. This is of primary importance in shaping ceramic wares. Some writers refer to the over-all property as plasticity (Hauser and Johnson 1942; Wilson 1936; Whitaker 1939; Norton 1948; Schwartz 1952), while others refer to it as workability (Norton 1938; Graham and Sullivan 1939; Henry 1942). The relative ranges of consistencies (D ÷ F) of bodies used in various molding operations are indicated in fig. 1. These data were obtained with a Gareis-Endell body tester (Henry 1943).

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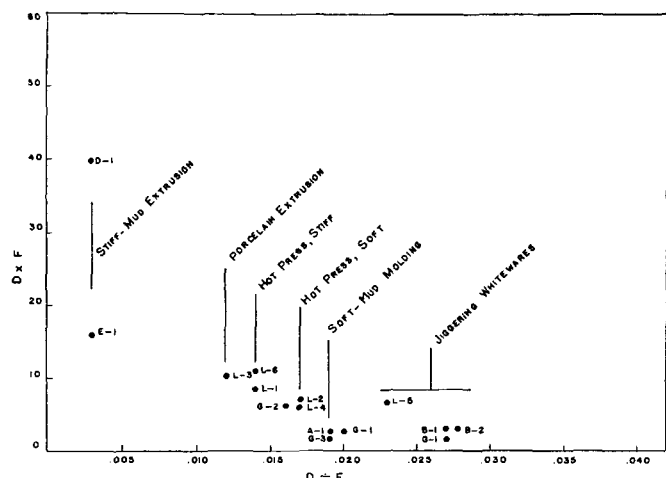


FIGURE 1. Relative softness (deformation in inches per pound of applied force) of bodies used in various molding operations.

Norton (1942) listed the variables in clay that influence the moulding properties: particle size, type of clay mineral, soluble salts and adsorbed ions, particle shape, and organic matter. In certain instances, particularly for brick clays and the like, the amount and kind of accessory minerals should be indicated as an additional factor. Norton stated (1942): "In the future the manufacturer of ceramics is going to demand a tailor-made clay which has all these variables under a reasonable degree of control. While at the present time it is not feasible to produce clay in large quantities with an exact control of properties, this can be done quite readily in the laboratory. For example, the grain size can be readily controlled by settling or centrifuging from a dilute suspension, the organic matter can be removed by an oxidizing treatment with hydrogen peroxide, and the soluble salts and adsorbed ions can be removed by leaching with an acid or by electro-dialysis. If these steps have been carefully taken, a clay can be produced of definite grain size, definite mineral content, a definite amount of adsorbed ions, and with controlled organic matter. It is this type of clay which will be more and more in demand by the manufacturer in the next few years."

Inasmuch as the clay producers for obvious reasons have not been able to accept Norton's challenge, the ceramic manufacturer is faced with a variety of problems in the utilization of clay:

(a) Purification of clays for ceramic use: The purification of relatively coarse-grained clays such as china clays does not present any particular difficulty. The use of settling troughs and, more recently, of centrifuges, makes possible a reasonable degree of mineral separation and gives a satisfactory particle-size control. The time probably will come, however, when it will be necessary to resort to flotation and other mineral-preparation techniques for concentrating clays from mixtures in which physical separation is not practical. Shaw (1937), Norman and Ralston (1940), and Kellogg (1947), have indicated the possibility of separating clay from silica, for example, of approximately the same grain size. Improved techniques for handling finer mineral fragments also will help in this direction.

In the matter of ball clays, the problem is more difficult, one of the major handicaps being the removal of water from the purified clay. Wilson and others (1935) investigated the possibility of removing the water gently without harming the plastic properties, by spray evaporation, but the method apparently is not economically feasible. Phelps (1950) has recently shown that certain ball clays can be purified by special air-floating procedures, and that these clays are equally clean or cleaner than the same clay washed through a 140-mesh screen.

Apparently little or no attention is being given to electrophoresis or electro-osmosis as methods of clay purification, in this country (Curtis, 1931).

(b) Aging and bacterial action: After the ceramic technologist receives his clay, purified or not, he mixes it with other ingredients and/or with water, and the clay or body develops its characteristic plastic properties. Some clays are used immediately after tempering; others are aged for various lengths of time. In the aging process, bacterial action is often more important than added hydration of the individual particles. Ogle (1901) and Stover (1902, 1903) appear to have been the first in this country to publish data on the effects of aging and of bacterial action. Glick and Baker (Glick 1935; 1936; 1936a; 1938; Baker and Glick 1936) counted and classified the bacteria present in some ceramic bodies. A bacteriologist, Glick was able to interpret the experimental evidence more ably than his ceramist predecessors. In his initial work, he showed that the workability of unsterilized clays improved as much in a week as that of sterile bodies in two months' time. Johnson, Postlewaite and Rittenberg (1949) recently showed the influence of bacteria in ceramic casting slips. They state "in spite of the difficulties, the general subject matter of the role of bacteria in ceramics would constitute a fruitful field of research."

(c) Modification of working properties: The earliest potters who felt the urge to experiment apparently realized that it was not always convenient simply to discard an unsatisfactory clay and search for a better one. Archeological evidence shows that clays early were mixed together and that it was also the practice to add nonplastics (pulverized rock) to clays when they were too sticky. Stetson (1952) reports that this tradition is so firmly entrenched that a present-day potter in Idlib, Syria, has been found still adding grains of limestone to his clay, although this is perhaps not necessary and now only results in limiting the temperature of firing of the body.

There is voluminous literature on the effects of additions of organic or inorganic chemicals on the plastic properties of clays. Early investigations were largely empirical, and the results were often contradictory. One of the first of this country to investigate these effects was Acheson (1904), who reasoned that the Children of Israel, as recorded in the fifth chapter of Exodus, were successful in substituting stubble for straw for the reason that the organic matter extracted from the stubble was important, not the fibres themselves. Acheson reported an experiment of adding an organic extract to a clay and drying at 100°C, thus obtaining a briquette which was stronger than the same clay untreated and fired to 1200°C. Phillips (1938) summarized the then-known means of improving the plastic properties of

clays and shales, including preheating and additions of acids, bases and salts. Cox (1951) recently called attention to preheating (calcination to 200 to 300°C) as a means of reducing the thixotropy of a clay difficult to deflocculate.

(d) Effect of amount and nature of exchangeable ions: The literature on ion exchange as a chemical phenomenon apparently originated with the work of Thompson (1850) and of Way (1850), and has been developed largely outside the field of ceramics. Von Liebig (1855), Gedroiz (1923), Mattson (1946), Hofmann and Bilke (1936), Kelley, Dore and Brown (1931), have influenced later ceramic investigators. Bayer (1929), a soil scientist, showed the effect of increasing amounts of lithium, sodium, potassium, magnesium, and calcium hydroxide on the pH, electrokinetic potential, electrical conductivity, and viscosity of dilute suspensions of an electrodialed colloidal fraction of Putnam silt loam. Bayer added quantities up to several times beyond the exchange capacity of his material, but naturally did not investigate many of the factors in which the ceramist would be interested. A number of ceramic investigators have contributed portions of a similar picture of the effect of the amount and kind of exchangeable ions on kaolinite; comparatively less has been done on illite.

Endell, Fendius and Hofmann (1934), Graham and Sullivan (1938; Sullivan and Graham 1940), Speil (1940), Siefert and Henry (1947), Harman and Fraulini (1940), Grim (1942) and others have discussed the ceramic effects of ion exchanges, mostly from the standpoint of the cations in the system. The effects reported by Barker and Truog (1938, 1939) on additions of sodium carbonate probably resulted from the formation of sodium clay.

Whether anions combine with ceramic clays to the same extent as do cations, has not been settled in the ceramic literature. Johnson (1949) states that no anion exchange has been reported for minerals of the montmorillonite group. He supports the concept that the exchange phenomena in kaolinite and some of those in montmorillonite arise from unsatisfied linkages resulting from the formation of fragmented particles.

Grim (1942) has mentioned that clay materials might also carry exchangeable anions but that almost nothing specifically is known of this property. However, he apparently was of the opinion that anion exchange might take place in clay minerals, for he questioned the existence of a diffused double layer on the basis that it would not satisfactorily explain the phenomenon of anion exchange.

Marshall (1949) showed from a study of titration curves that both the hydroxyl ions and the cations are fixed in non-ionized form over a broad range of alkalities. The results of titration carried out by using mixtures of hydroxyl and chloride ions supplied evidence to demonstrate that weakly acidic groups were responsible for this behavior. The presence of a neutral salt greatly increased the amount of base needed to obtain a given pH. Mattson and co-workers (Mattson and Gustafsson 1935; Mattson and Wiklander 1937) devoted considerable space to discussions of anion and cation reactions, particularly from the standpoint of Mattson's concepts of exchange acidity, exchange alkalinity and exchange neutrality. The pH values of aqueous suspensions of electrodialed Florida kaolin containing various amounts of NaOH or HCl are given in figure 2. When NaCl is present, the pH is shifted, resulting in exchange acidity, shown to the right of the point of exchange neutrality (E.N.) and exchange alkalinity, to the left (Henry and Taylor 1938).

Murphy (1939) recorded that finely ground kaolinite takes up phosphate ions extensively at very low pH values. This was confirmed by Stout (1939) who showed by X-ray and chemical studies that the hydroxyl groups were made accessible by fine grinding, and that the phosphates reacted with loss of water. Marshall criticized these results and gave the opinion that this finely ground material was no longer kaolinite but a permutite-like material. However, the validity of Marshall's assumption that fine grinding destroys the crystalline structure may be questioned.

Dean and Rubins (1947), in experiments of phosphate adsorption by kaolinite clays, reported that the relatively rapid adsorption of ions from dilute solutions is a property of the Al-OH groups at the crystal edges. It was found that the anion adsorption capacity was approximately equal to the cation exchange capacity for kaolinite clays. This would naturally be the case where broken bonds of OH-Al, O-Al and O-Si on the

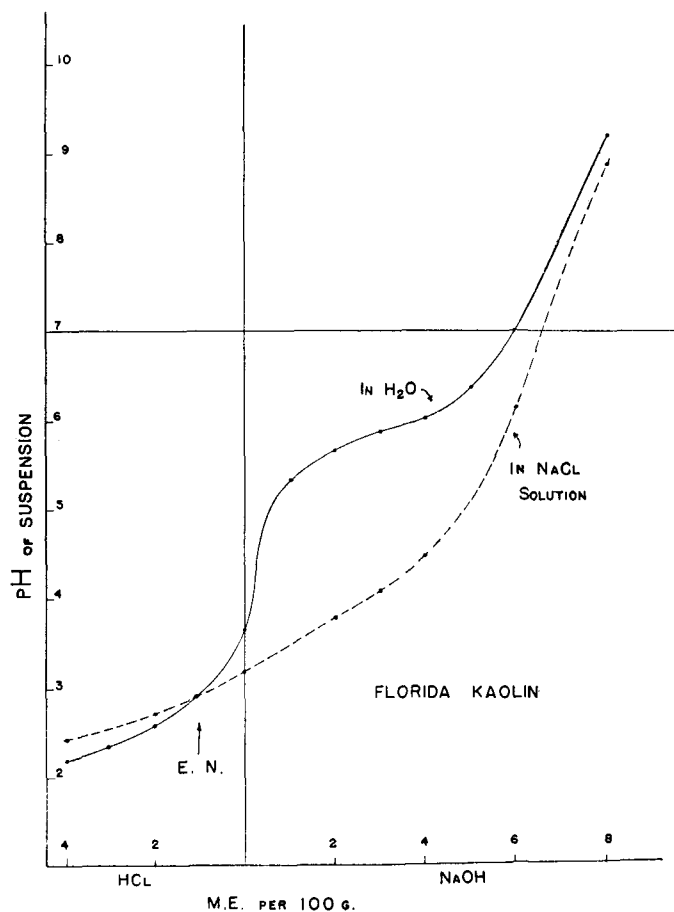


FIGURE 2. Titration curves of electrodialed Florida kaolin in distilled water and in N/2 NaCl solution, showing exchange acidity, exchange alkalinity, and exchange neutrality (E.N.).



edges are responsible for the base exchange and similarly broken bonds of Al-OH, Al-O and Si-O are responsible for the anion exchange. In montmorillonite-type minerals the anion absorption would amount only to a small fraction of cation exchange capacity if the latter is predominately due to negative charges on the planar surfaces. On this basis, the anion exchange capacity of illites would likewise be a fraction of the cation exchange capacity. However, if the potassium ion which is in the fixed positions balances the excess lattice charge, then the anion exchange capacity can be approximately equal to the cation exchange capacity. Marshall (1949) stated: "In the montmorillonite-beidellite and hydrous mica clays we have permanent negative charges upon the planar silicate surfaces. At the edges, however, Si-OH and Al-OH groups are present. The former are weakly acidic and contribute to the increase in exchange capacity in the alkaline media. The latter provides a site for the anion adsorption. In the kaolinite clays there is little or no permanent charge. Accidental anion or cation absorption is of predominant importance. Since the ratio of the Al-OH to Si-OH at the edges is now 1:1 whereas in montmorillonite it is 1:2, anion adsorption comes even more predominantly in the picture. Dean and Rubins' observation that  $\text{PO}_4^{--}$  and  $\text{SO}_4^{--}$  adsorption are approximately equivalent to cation exchange capacity for kaolinite clays fits very neatly into this picture."

Prabhu (1950) presented evidence that chloride ions are held less firmly than sulfate, and sulfate less than phosphate, reasoning from observed displacements of the point of exchange neutrality. In kaolinite, anion exchange capacity with respect to the phosphate ion was found to be almost equal to the base exchange capacity; in the case of illites it was slightly less, but it was about one-third the base exchange capacity value in the case of montmorillonite.

The practical importance of the effects of anions as well as of cations is brought out by a series of papers stressing the ions introduced by water, into ceramic bodies. Phelps (1950) discussed water as a raw material, Kahler and Wantz (1950) considered specifically the problems of water in porcelain enameling, and Smith (1951) showed the effect of the quality of the water in the manufacture of ceramic wares and porcelain enamels. Smith pointed to the need for controlling the anion as well as the cation. Ordinary zeolites, which cause simply a base exchange, are not enough. Demineralizers now available remove anions as well as cations, and make unnecessary the addition of extra deflocculants to counteract the  $\text{SO}_4^{--}$ ,  $\text{NO}_3^-$ , or  $\text{Cl}^-$  otherwise introduced by the water. They also make it unnecessary for a company to produce distilled water for its casting slip.

Some specific effects of  $\text{SO}_4^{--}$  and of  $\text{F}^-$  in ceramic clays have been reported by Johnson and Hughes (1948) and by Kingery (1951).

(e) Clays as colloidal electrolytes: Hartley (1935) has stated "Charged colloids divide themselves into two fairly well-defined classes—on the one hand a class where the bulk of the particle is made up of insoluble materials in regard to which there is no equilibrium and whose charge is due chiefly to preferential adsorption of foreign ions—and on the other hand, the class in which

the particle is made up of a definite ionizing compound with regard to which there is true equilibrium and whose charge is due to ionization of this compound." Marshall and Krinbill (1942) point out that the term colloidal electrolyte applies only to the second class, and that according to this definition kaolinite cannot be considered a colloidal electrolyte since the exchange capacity is a function of particle size. However, knowledge of the theoretical ionization of the postulated compounds formed between ions and the clay often is helpful in explaining ceramic-colloidal phenomena. Mattson (1937; Mattson and Kwang-Chiung Hov 1937) early considered clays as colloidal electrolytes. Although his postulation of the amorphous nature of the colloidal fraction of clays has had to be modified in view of knowledge that crystalline structure extends into the colloidal size range, his concepts of acid, base and neutral salt reactions, resulting in exchange alkalinity, exchange acidity, and exchange neutrality, may help indicate the relative strengths with which various ions are adsorbed on clays. Johnson and McCartt (1952) have very recently reported the use of the flame spectrophotometer in determining the concentration of cations in solution and those adsorbed, from mixtures of various cations, and have established an order of relative strengths of adsorption. It is noteworthy that Johnson and McCartt place hydrogen at such a position that it does not displace calcium and magnesium, which would indicate that electro dialysis is a better technique for purifying clays than is acid leaching.

The colloidal-chemical aspects of the clay-water system have been detailed by Hauser (1941), Johnson (1943) and Norton and his associates (Johnson and Norton 1941; 1941a; 1942; Johnson and Lawrence 1942; Norton and Johnson 1944; Norton, Johnson, and Lawrence 1944; Kocatopcu 1946; Norton 1948; Coughanour and Norton 1949; East 1950; Kingery 1951; Schwartz 1952), and others.

(f) Slip casting: Slip casting, the process in which clays or mixtures of clays and non-plastics are diluted with water to about the consistency of cream, seems to have received more attention with respect to ion-exchange control than has the plastic state. Norton and his co-workers, Russell, Mohr and Rice (Russell and Mohr 1944; Russell, Mohr and Rice 1949), Phelps (1947; 1947a; 1947b; 1947c; 1947d; 1947e; 1948, 1948a) and others have covered this subject rather thoroughly. Many a plant ceramist would undoubtedly like to have a clay slip which could be cast in a deflocculated state, with a minimum of water, then flocculated by some simple means.

The ceramist finds a suite of special problems in applying control to casting slips. He must watch the degree of deflocculation in order to control the thixotropic behavior of the slip. In solid casting, bodies must be encouraged to jell at least somewhat in order to permit removal of the core before shrinkage causes the body to cling to the core. The permeability of the cast wall is particularly important in casting thick-walled pieces.

(g) Chemical treatment: Chemical treatment of ceramic clays and bodies to improve their plastic and drying behavior has not received as much acceptance as it would seem to warrant. This may be due partly to the fact that vacuum extrusion (Everhart, Austin,

and Rueckel, 1932) was introduced at just about the time that interest in chemical treatment as an ion exchange phenomenon was being aroused. The results of de-airing were spectacular enough to overshadow the improvements resulting from chemical treatment. Dinnerware manufacturers use chemical additions for improved control of jiggering bodies. This is particularly important because of the trend toward increased use of automatic jiggering. Automatic machines are as yet incapable of adjusting themselves to minor variations in the working properties of the bodies. Brick manufacturers, however, who work with up to 100 percent clay content masses, do not seem to have investigated the possibilities offered by a combination of chemical treatment and de-airing.

Along with discussions of the control of plastic properties of clays by chemical additions, the advantages offered by emulsions have been considered. Straight (1940; 1941; 1945) found that approximately one pound of kerosene (in a kerosene-soap emulsion) would take the place of 80 pounds of pugging water, that dryer shrinkage was reduced 50 percent, dried strength was increased, and fired absorption was decreased. Grupelli (1944) also pointed to the advantages of using emulsions, indicating (as had Straight), reduced power for pugging as a result of the internal lubrication.

(h) Clays as suspending or binding agents: An important use of clays is in stabilizing suspensions of non-plastics and of pulverized glass (frit) in the application, by dipping or spraying, of glazes to clay bodies and vitreous enamels to metals. Harman, Schaffer, Blanchard and Johnson (1944) studied the factors involved in glaze slip control.

A still different application of clays in ceramics is their use in small amounts to bind relatively large grog particles in the manufacture of refractories. The problems here are very similar to those in the production of synthetic moulding sand for foundry work, a borderline ceramic useage, and have been effectively described, from the physical point of view, by Grim and Cuthbert (1945, 1946).

(i) Differential thermal analysis: The ceramic technologist has made wide use of differential thermal analysis in recent years. Norton (1939) was apparently one of the first to use this technique in identifying and classifying American ceramic clays. Speil, Berklehamer, Pask, and Davies (1945) gave a thorough discussion of the previous work, apparatus, and applications to clay work, and Grim and Rowland (1942; 1944) used this extensively with clays. Gruver (1948) called attention to the advantages of using containers having a minimum heat capacity, and was able to detect heat effects which would otherwise be overlooked. Stone (1952) recently presented evidence that the decomposition temperature of the kaolinite group of minerals increases with increasing pressure of water vapor in the atmosphere and that the decomposition reactions of these minerals are reversible at their equilibrium temperatures. He indicated the order of magnitude of the heat of decomposition of dickite.

(j) Drying of clay wares: The technology of drying clay wares involves applications of colloid chemistry and of mineralogy. In essence, drying is controlled by (1) the rate of diffusion of water through the clay body to

the surface, and (2) the evaporation of water from the surface.

Knowledge of the drying strength, that is, the change of plastic tensile strength (cohesiveness) of the clay with change in water content, is essential in solving problems of drying losses resulting from cracking. The importance of the water films on and between clay particles cannot be overestimated. In certain instances, kaolinitic clay pieces while drying shrink to dimensions smaller than the corresponding lengths when dry: apparently the clay flakes undergo a relaxation as the last portions of water are removed (Norton, 1933).

Figure 3 shows the relationship between water content and drying shrinkage for electrolyzed (H) and sodium-saturated (Na) Tennessee ball clay (Henry and Siefert, 1941).

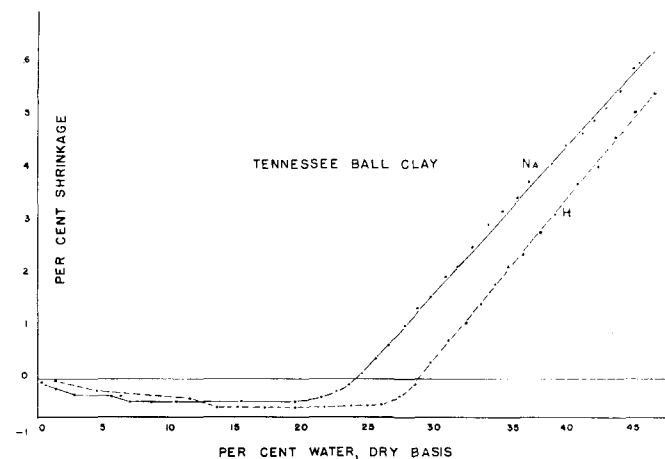


FIGURE 3. Water content and linear shrinkage relationships during drying of a Tennessee ball clay.

It is believed that clay test pieces have greater plastic tensile strength when the clay is flocculated, but higher dry strength when the clay has been deflocculated. A more complete study of the change of strength with condition, ion atmosphere, and water content seems desirable. The plastic tensile strength of such test pieces in-

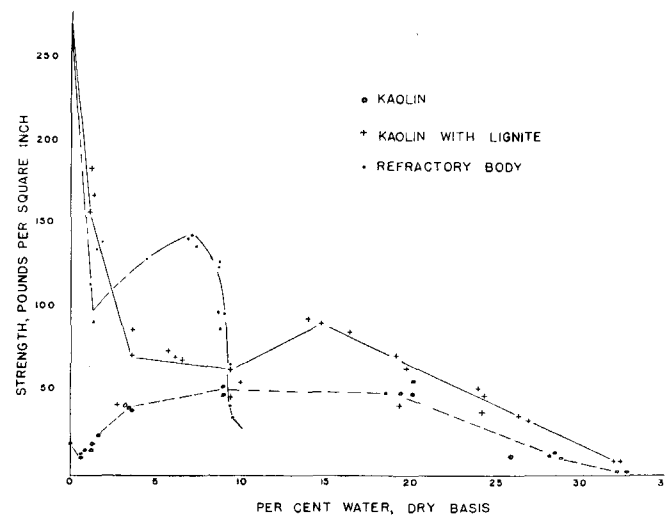


FIGURE 4. Relative plastic tensile strength as influenced by water content.

creases as the water content is decreased, during drying, but does not necessarily do so in a regular manner (fig. 4).

(k) Atomistic approach: In the last few years W. A. Weyl and his associates have accumulated considerable information on the behavior of surfaces of oxides which contain cations of zero or very low polarizability, namely, water,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$ . Water (Weyl, 1951) has certain unique properties which were explained on the basis that a proton, since it has no electron cloud surrounding its nucleus, has zero polarizability and can penetrate into other electron clouds because there is no electron-electron repulsion. This should be compared with the combination of an  $\text{Na}^+$  ion with a  $\text{Cl}^-$  ion, which results from the Coulomb attraction forces, but in this instance the two ions also exert repulsive forces upon each other; in close proximity the two positive nuclei and the two negative electron clouds repel one another.

Weyl and his associates recently pointed out several unusual chemical reactions which take place at a freshly formed surface of silica. The reactions were anticipated because of the strong demand for screening on the part of the highly charged and only slightly polarizable  $\text{Si}^{++++}$  ion. It has been established that  $\text{Si}^{++++}$  ions in glasses (Weyl, 1951a) and in crystalline silicates (Hauth 1951) are surrounded by at least four  $\text{O}^-$  ions. Such complete screening of the  $\text{Si}^{++++}$  is not possible within a surface layer. As a result, a freshly formed surface of silica, either when obtained by the fracture of quartz or by the dehydration of a silica gel, reacts chemically with its environment (Weyl, 1950).

The greater the charge of an ion and the more its polarizability, the more it contributes to the surface energy of a system where it appears in a surface. Normally, ions of the type of  $\text{Si}^{++++}$  do not appear at a surface (at least not in an equilibrium surface). According to Weyl, a freshly formed surface lowers its free energy by two processes, one an instantaneous process, and another which is time-consuming because it involves the cooperation and movement of many ions. The instantaneous process involves a change of the electron density distribution of the surface ions. Compounds which contain only highly polarizable ions ( $\text{PbI}_2$ ) can lower their surface energy by this instantaneous process. For ceramic substances such as clay or quartz this process is of little significance because the cations  $\text{Si}^{++++}$ ,  $\text{Al}^{+++}$ , etc., are not sufficiently polarizable to be deformed in the same way that  $\text{Pb}^{++}$  ions can be deformed.

The second process is described as a change of the geometry of the surface structure in which the anions are, so to speak, pushed to the front and the cations are pulled into more covered positions. This change has to have a depth action in order to allow a gradual transition from the normal to the distorted structure of the crystal.

P. A. Marshall<sup>1</sup> observed strong electrical charges when a silica gel or an alumina catalyst after dehydration at 150-400° C was brought in contact with water. The occurrence of excess electrical charges indicates that the screening demands of the  $\text{Si}^{++++}$  are not satisfied by the adsorption of water molecules but that the demand for the more polarizable hydroxyl ions causes the silica

to react with the water and cover its surface with  $\text{OH}^-$  ions and, thus, release protons or hydronium ions.

The fact that the more polarizable  $\text{OH}^-$  ions are better screeners than the less polarizable water molecules explains the observation of VanPraagh (1939) who found that ignited quartz produced a distinctive acidity when immersed in pure water. VanPraagh emphasized that this acidity could not be explained on the basis of very low solubility of silica in water and the dissociation constant of the silicic acid. He assumed, therefore, that impurities, such as strongly adsorbed carbon dioxide might be responsible for the effect. Recently, D. P. Enright and W. A. Weyl (1952) demonstrated that the pH of a suspension of quartz in water can undergo reversible changes if the quartz powder is allowed to settle. During the sedimentation process adjoining quartz particles assume positions under which they can share  $\text{OH}^-$  ions, causing the acidity of the supernatant liquid to decrease. If the settled powder is stirred, a new equilibrium is obtained within a few minutes and the pH of the slurry is found to decrease by about 0.2 of a unit.

Lindenthal (1952) showed, in continuation of Enright and Weyl's work, that the addition of powdered quartz (pottery flint) to distilled water increased its electrical conductivity. He suggested that the screening demands of the surface cations of quartz particles create enough energy to dissociate the water molecule and to attract  $\text{OH}^-$  ions. This would also explain the fact that particles of quartz immersed in water assume a negative charge. He explained the increase in conductivity and certain viscosity changes in suspensions of pottery flint, in water and in glycerol, on the basis of the polarization theory, and suggested that screening can explain electrophoresis, electro-osmosis, streaming potential, and the Dorn effect (sedimentation potential) in quartz suspension.

With highly polarizable ions, on the other hand, the strong asymmetrical force fields at the surface may be readily adjusted, and the need for  $\text{OH}^-$  ions from  $\text{H}_2\text{O}$  for screening is proportionately reduced. Thus, Saunders, Enright, and Weyl (1950) showed that a porous clay film would no longer absorb water instantaneously after being treated with  $\text{Ni}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Hg}^{++}$  or similar ions with incomplete outer electron shells. Contact angles up to 70° could be observed for a short period for drops of water on  $\text{Hg}^{++}$  and  $\text{Pb}^{++}$  clays.

Is the increased electrical conductivity in distilled water, on the addition of dry electro-dialyzed clay, to be explained on the same basis? Gruver<sup>2</sup> has reported that the pH of a dilute suspension of electro-dialyzed kaolinite decreased about 0.2 pH when the suspension was allowed to settle, and returned to its original lower value when the suspension was again stirred. The pH increased as soon as the clay particles had settled below the electrodes of the pH meter. In this instance, did the pH drop because released  $\text{OH}^-$  ions neutralized some of the  $\text{H}^+$  ions in the supernatant liquid, or because the  $\text{H}^+$  containing micells were removed from the neighborhood of the electrode? This may be compared with the statement of Hauser and Johnson (1942) regarding electro-dialyzed clay in distilled water: "Because of the

<sup>1</sup> Personal communication (Department of Mineral Technology, The Pennsylvania State College, State College, Pennsylvania).

<sup>2</sup> Personal communication (Division of Ceramics, The Pennsylvania State College, State College, Pennsylvania).



positions which the hydrogen counter ions take, all of the counter charges occur within the hypothetical water hull." The question then becomes whether the ultimate pH of dry electrolyzed clay is caused by hydrogen ions introduced by the dry clay and dissociated from it, or whether they result from the dissociation of water somewhat as in the case of the pottery flint. Evidence favors the latter view.

*Firing of Clays.* Discussion of the technology of clays in the field of ceramics would not be complete without consideration of the effect of heat on clays. Industrially, one observes shrinkage and change of porosity, but what is back of this? The firing behavior of a clay at a given temperature is determined by its mineral constitution, particle-size distribution, firing atmosphere, and, very greatly, by the amount and kind of accessory minerals present or added. Decomposable minerals, for example, contribute to the bloating of clays in the production of light-weight aggregate for concrete.

It is of particular interest to note that when clays or ceramic bodies are heated, a second plastic stage (pyroplastic condition) is reached, beginning perhaps at 700-800°C. The relative amounts of liquid and solid phases present, and the viscosity of the liquid phase, largely determine the pyroplastic properties.

McDowall and Bose (1951), and Wiechula and Roberts (1952) have discussed this subject in considerable detail.

In this field, also, the atomistic approach is beginning to be felt. Weyl (1951b) postulates that it is the mutual repulsion between unscreened cations which controls the melting of simple binary compounds. In order to melt, a crystal such as NaCl has to have sufficient thermal energy to allow one Na<sup>+</sup> ion to pass another Na<sup>+</sup> ion without Cl<sup>-</sup> ions between them. The energy requirement for overcoming the cation-cation repulsion is high if the cations have strong potential fields and their polarizability is low. The polarizable non-noble gas-like ions, on the other hand, exert much weaker repulsion forces upon one another. The melting points of groups of corresponding compounds are lower for the one which contains the polarizable type ion than for the one which has a non-polarizable ion. Keeping this relationship in mind, one can understand why ZnO melts at 1975°C whereas MgO melts at 2800°C in spite of the fact that Mg<sup>++</sup> ions and Zn<sup>++</sup> ions have identical excess charges and are approximately the same size.

Weyl and Enright (1952) report that the beginning of a sintering reaction is dominated by the surface structure of the individual crystal. Cations of very low polarizability and relatively high potential fields are not likely to appear as constituents of equilibrium surfaces. They become covered with molecules adsorbed from the atmosphere or they develop an electrical layer consisting of O<sup>-</sup> ions in the outer layer, backed up by cations. The result is mutual repulsion between electrically neutral particles. The formation of such an electrical layer is responsible for the fluffiness of MgO prepared by calcination of MgCO<sub>3</sub> or Mg(OH)<sub>2</sub>. This condition inhibits contact and sintering, but can be overcome if cations of a much higher polarizability than that of the Mg<sup>++</sup> ion are introduced. Non-noble gas ions such as

Zn<sup>++</sup> or Fe<sup>+++</sup> ions are much more likely to participate in the surface layer of their oxides and, as such, they facilitate contact between the crystal faces of adjoining particles, which is the prerequisite for recrystallization. Thus, the presence of "mineralizing agents" removes the double layer and helps establish direct contact between individual crystals.

Weyl and Enright also show examples in which the introduction of the proper impurity into the crystal makes it possible to counteract the formation of vacant lattice sites and, thus, to retard sintering of those oxides which form semiconductors by either thermal dissociation or by oxidation-reduction processes. This is an instance in which the addition of an impurity raises the sintering temperature of an oxide.

*Summary.* The technology of clays in ceramics involves many variables, most of which relate to the clay-water system. Directly associated are problems in colloid chemistry, mineralogy, physical chemistry, and atomistic chemistry. Related problems include those of aging, bacterial action, and the effects of varying amounts of the possible anions and cations which may be present or added, and, in addition, all these apply over a wide range of moisture contents and of consistencies. After the shaping of the ceramic article from a clay body at one of these consistencies, the over-all effect of these variables on drying and firing are involved.

It is the conviction of many investigators in the field of ceramics that ceramic manufacturing can be controlled at every step, and that not only can further improvements be made, but that radically new methods of manufacturing ceramic wares can be introduced by applying a combination of colloid chemistry and atomistic principles. Detailed systematic research will be necessary to obtain all the information needed for complete control of each of the various steps in the production of ceramic wares. Pure clay minerals must be studied further from every possible aspect: mineralogically, by X-ray, by electron micrograph and electron defraction, by infra-red analysis, by chemical analysis, in terms of ultimate and effective particle sizes, and with respect to ion-exchange reactions. The corresponding effect of these variables on the electrical charge, and its effect, in turn, on workability, viscosity, and drying and firing behavior must be noted. Studies may then be made on mixtures of clay minerals in selected proportions and under controlled environmental conditions. This appears to be a long and tedious program, but the results should be well worth the effort, in the benefits to be derived by the ceramics industries.

## DISCUSSION

### W. J. Knapp:

Are there any opinions on the forces which act between particles in a clay-water mixture? If we knew what those forces were, we could explain plasticity.

### E. C. Henry:

If an alumino-silicate can have such a demand for hydroxyl ions that it will dissociate water (to make hydroxyl ions available for screening the cations) one would expect this to lead to strong tensile force between particles. If, on the other hand, one uses highly polarizable ions at the surface, that is, treats the clay so it essentially is coated with these; then there will not be the need for the hydroxyls. In other words, we would predict that the plastic tensile strength of a clay should be high if the clay is pure and

does not have polarizable ions, and should be lower if the surface contains polarizable ions.

**F. N. Hveem:**

Why must it be assumed that there are any measurable forces between particles in a clay-water system? In the field of portland-cement concrete mixtures, the phenomena of mobility and plasticity are also of concern. Ninety percent of the technique of designing a concrete mix is how to make it sufficiently plastic without using water. This is very close to the technique of preparing clays for ceramic purposes. Water causes volume change and shrinkage in clays, and produces lower strength and other difficulties in concrete; so we must make a plastic mass with the minimum of water. Recently, for durability purposes, techniques were developed for introducing air-entraining agents, which entrain the concrete minute air globules. The plasticity of concrete is vastly increased by the mobility of these air bubbles, which we might imagine to function as miniature ball bearings. What use can be made of fundamental information in predicting the performance of clays in the presence of water?

**E. C. Henry:**

By not using water we can lower the cohesive forces and the internal friction. H. R. Straight (1940; 1941) used an emulsion of kerosene and soap to obtain internal lubrication of a clay mix. One pound of emulsion replaced 50 to 80 pounds of water and the power required for the pugging and extruding of the clay body was very greatly reduced. He probably had a clay that was very fine-grained and had ample plasticity; perhaps he did not need to develop much plasticity from the clay-water interface, but apparently the attractive forces or the frictional forces between particles were greatly reduced by using a non-polar liquid. This could have been either a chemical effect, mechanical lubrication, or both.

**W. J. Knapp:**

Norton (1952, pp. 77-80) postulates several simple forces acting between clay plates in the water medium. A force of interfacial tension or capillary attraction exists. The other force he postulates is related to the charge on the particle. These two forces are counterbalanced one with the other to form a system of forces. Does the same sort of force act between glass plates if they are nested one on the other and water poured over them?

**W. T. Cardwell, Jr.:**

We became interested in what the cement technologists had done to reduce permeability by approaching a condition of minimum voids and we tried to relate this to lowering filter loss. We tried to control particle-size distribution to cut down the filter loss, but the difficulties encountered were in connection with the forces between the particles. The small montmorillonite clay particles will not pack close to anything else or to each other. A suspension of ultracentrifuged bentonite placed in a filter cell with pressure applied at the top will not form a true filter cake; the particles of the very fine bentonite will not pack. Ordinary bentonite placed in the filter cell will form a conventional filter cake.

**J. W. Jordan:**

In connection with the filter problem, the American Petroleum Institute filter-loss outfit is very satisfactory for evaluating the permeability. A plot of viscosity versus filter loss will be essentially similar to the graph of swelling versus filter loss with one exception. When attapulgite is tested, a viscosity comparable to that of bentonite is obtained but the filter loss is off the chart. This is probably related to particle shape. Attapulgite particles are needle-like and when they are matted on the bottom of a filter cell they act like straws through which the water permeates. The montmorillonites with their flake forms act like sheets of paper lying flat.

**F. N. Hveem:**

Hardy (1926) reported that in a number of tests under a wide variety of conditions it was demonstrated that water has no lubricating powers whatsoever on pure uncontaminated surfaces; therefore any lubricating effect developed by water must be in relation to some other compound or element, frequently organic. Tests were made on quartz plates, glass plates, metals, and a wide variety of other materials. With the exception of some such substances as ebonite and rubber, the resistance to sliding friction of surfaces in contact with a film of water was no less than it was on a dry surface. Has anyone any comments on the relation of these statements to the plasticity of clay through the addition of water?

**E. C. Henry:**

Perhaps Hardy was correct in his statements about surface films; but if one has, in addition to the surface films, an excess of water, then he has a two-phase system. The water is the phase which imparts the mobility to the system.

**F. N. Hveem:**

In our laboratory, in measuring internal friction of soil masses, we invariably found that with the addition of water, friction resistance begins to diminish considerably before the voids are filled.

**E. A. Hauser:**

Is there any comment on the idea that soil problems ascribable to soil permeability, water sensitivity, and other characteristics, appear to be amenable to treatment by small amounts of chemicals?

**R. C. Mielenz:**

In order to effect substantial changes in permeability there would be required substantial amounts of chemicals so as to alter the surface characteristics of the very fine undisturbed soil.

**F. N. Hveem:**

I believe that Hewitt Wilson made the statement that the fluidity of a clay slip could be altered and increased as much as 300 percent by the addition of 0.1 percent of  $\text{Na}_2\text{CO}_3$  to the mixture. This seemed to be a very small amount. In our work a sample of soil was taken from a pit near Los Angeles. Tests on apparently identical samples taken side by side out of the same deposit gave quite different results. A complete sieve analysis showed no difference. The laboratory found that they were identical except that the sample which swelled more and had lower stability, contained 0.05 percent sodium sulfate. We added a very small amount of sodium sulfate to the other sample, and it promptly swelled more and the stability was lowered, although not to the same degree.

**R. L. Stone:**

Sulfate is by no means a stranger to the ceramic people. The presence of soluble sulfate will definitely alter the plastic characteristics of a clay mass. The general practice to offset the effects of soluble sulfate is to add an appropriate amount of  $\text{BaCO}_3$  which will precipitate the sulfate ion as the insoluble  $\text{BaSO}_4$ . Without this treatment, it is impossible to deflocculate many clays for casting. The  $\text{BaCO}_3$  also prevents formation of a sulfate scum during drying.

**J. M. Catterton:**

Thinning action of  $\text{BaCO}_3$  on a clay slurry can also result from the removal of calcium ion as calcium carbonate. Has anyone studied the relative effect of various ions on the viscosity of a slurry?

**E. C. Henry:**

Baver (1929) made a rather thorough survey of the effect of the amount and kind of cation on the viscosity of a clay suspension.

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