Clays are used in the ceramics industries largely because of their
current to the moulding and drying properties of the wares
being produced; many clays, such as the flint clays, are used be-
cause 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 tech-
nologist 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 phe-
nomena 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 func-
tions is generally served. Most clays, alone or in mix-
tures, 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 filter 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 prac-
tice 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 re-
ports of empirical investigations and of practical ap-
lications, much of the basic theory has come from the
fields of colloid chemistry, mineralogy, physical chem-
istry, 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
clay 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 con-
trol is concerned.

One of the difficulties facing the layman in attempting
to obtain a systematic picture of clay technology in
earm 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 unsuit-
for another; there apparently are almost no entirely
good or bad ceramic clays.

This condition perhaps explains much of the con-
fusion and contradiction found in the reports on investi-
gations 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 re-
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 ben-
ficial or detrimental.

Ceramic classification of clays is undergoing a revi-
sion. 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 fire-
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 identifica-
tion 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 measurable mobility. The
ceramist, however, is vitally interested also in still a
third factor, the extensability; 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 (Hau-
sen 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).
Norman and Kalston (1940), and Kellogg (1947), have also proved techniques for handling finer mineral fragments which physical separation is not practical. Shaw (1937), indicated the possibility of separating clay from silica, and gives a satisfactory particle-size control. The 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 stated "in spite of the difficulties, the general subject matter of the role of bacteria in ceramics would constitute a fruitful field of research."

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.

(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. Stetsen (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 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. Baver (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 electrodialyzed colloidal fraction of Putnam silt loam. Baver 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, Feudius and Hofmann (1934), Graham and Sullivan (1938; Sullivan and Graham 1940), Speil (1940), Siefert and Henry (1947), Harman and Faulini (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 alkalinities. 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 electrodialyzed 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
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-heidellite 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 PO_4^{3-} and SO_4^{2-} 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. Deminerizers now available remove anions as well as cations, and make unnecessary the addition of extra defloculants to counteract the SO_4^{2-}, NO_3^-, or 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 SO_4^{2-} and of 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 Krinbll (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-Chung 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 electrodialysis 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 Lawrenece 1942; Norton and Johnson 1944; Norton, Johnson, and Lawrence 1944; Koecatopen 1946; Norton 1948; Conghanour 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; 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 defloculation 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. Dinner-
ware manufacturers use chemical additions for improved
control of jiggering bodies. This is particularly impor-
tant because of the trend toward increased use of auto-
matic 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 prop-
ties 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 emul-
sions, indicating (as had Straight), reduced power for
pugging as a result of the internal lubrication.

(h) Clays as suspending or binding agents: An im-
portant 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, Blancliard
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 prob-
lems here are very similar to those in the production of
synthetic moulding sand for foundry work, a borderline
ceramic usage, and have been effectively described, from
the physical point of view, by Grim and Cuthbert (1945,
1946).

(i) Differential thermal analysis: The ceramic tech-
nologist has made wide use of differential thermal anal-
ysis 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 increas-
ing pressure of water vapor in the atmosphere and that
the decomposition reactions of these minerals are revers-
able 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 electrodialyzed (H) and so-
dium-saturated (Na) Tennessee ball clay (Henry and
Siebert, 1941).

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 con-
dition, ion atmosphere, and water content seems desir-
able. The plastic tensile strength of such test pieces in-

![Figure 3](image-url)
creases as the water content is decreased, during drying, but does not necessarily do so in a regular manner (fig. 4).

(k) Atomic model 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, SiO₂, and Al₂O₃. 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 Na⁺ ion with a 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 Si⁴⁺ ion. It has been established that Si⁴⁺ ions in glasses (Weyl, 1951a) and in crystalline silicates (Hauth, 1951) are surrounded by at least four O⁻ ions. Such complete screening of the Si⁴⁺ 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 Si⁴⁺ 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 (PbI₂) 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 Si⁷⁺, Al⁷⁺, etc., are not sufficiently polarizable to be deformed in the same way that 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 definite action in order to allow a gradual transition from the normal to the distorted structure of the crystal.

P. A. Marshall¹ 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 Si⁴⁺ 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 OH⁻ ions and, thus, release protons or hydronium ions. The fact that the more polarizable OH⁻ ions are better screeners than the less polarizable water molecules explains the observations 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 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 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 OH⁻ ions from H₂O 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 Ni²⁺, Mn²⁺, Hg²⁺ 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 Hg²⁺ and Pb²⁺ clays.

Is the increased electrical conductivity in distilled water, on the addition of dry electrodialized clay, to be explained on the same basis? Gruver² has reported that the pH of a dilute suspension of electrodialized 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 OH⁻ ions neutralized some of the H⁺ ions in the supernatant liquid, or because the H⁺-containing micelles were removed from the neighborhood of the electrode? This may be compared with the statement of Hauzer and Johnson (1942) regarding electrodialized clay in distilled water: "Because of the

¹ Personal communication (Department of Mineral Technology, The Pennsylvania State College, State College, Pennsylvania).
² 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 electrodialized 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 concretes.

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⁺ ion to pass another Na⁺ ion without Cl⁻ 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 Mg²⁺ ions and Zn²⁺ 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⁻ 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 smoothness of MgO prepared by calcination of MgCO₃ or Mg(OH)₂. This condition inhibits contact and sintering, but can be overcome if cations of a much higher polarizability than that of the Mg²⁺ ion are introduced. Non-noble gas ions such as Zn⁺⁺ or Fe⁺⁺ 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 these 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, such as, 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
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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-saturating 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 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.

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 power 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 Na₂CO₃ 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 BaCO₃ which will precipitate the sulfate ion as the insoluble BaSO₄. Without this treatment, it is impossible to defloculate many clays for casting. The BaCO₃ also prevents formation of a sulfate scum during drying.

J. M. Catterton:
Thinning action of BaCO₃ on a clay slurry can also result from the removal of calcium ions as calcium carbonate. Has anyone studied the relative effect of various ions on the viscosity of a slurry?

E. C. Henry:
Baver (1926) made a rather thorough survey of the effect of the amount and kind of cation on the viscosity of a clay suspension.

SELECTED REFERENCEs
Acheson, E. G., 1904, Egyptianized clay: Am. Ceramic Soc. Trans., v. 6, pp. 51-64.
Cox, P. E., 1951, How to reduce thixotropy in clays: Ceramic Age, v. 58, no. 2, pp. 30-31.


Hofmann, U., and Birke, W., 1936, Uber die innerkrystallinelle Quellung und das Basen-austauschvermogen das Montmorillonits (Inner crystal swelling and base-exchange capacity of montmorillonite): Koloid-Zeitschr., v. 77, pp. 238-251.


Kingery, W. D., 1931, Note on the effect of fluoride ions on a clay suspension: Am. Ceramic Soc. Jour., v. 34, no. 8, pp. 242-244.


Mattson, S., 1929, Laws of soil colloidal behavior (24 parts to date, appearing at intervals) : Soil Sci., v. 28, p. 179 (I, 1929) to Soil Sci., v. 61, p. 313 (XXV, 1940).


McDonnell, I. C., and Rose, W. C., 1951, Determination of the pyroplastic deformation in the firing of ceramic bodies: British Ceramic Soc. Trans., v. 50, no. 11, pp. 506-516.

Murphy, H. F., 1939, The role of kaolinite in phosphate fixation: Hilgardia, v. 12, p. 293.
