

FIG. 1—Crystal structure of Hydrated Silica.

Scientific Research in Ceramics

By POL E. DUWEZ

SCIENTIFIC research in the field of ceramics may appear as a rather strange subject to many engineers and physicists. The ceramic industry is exceedingly old. For example, the manufacture of artistic porcelain had reached a remarkable state of perfection long before any scientific research had penetrated the field of industry. Very little scientific knowledge was necessary to the Chinese, Sevres, or Delft artist, but now the field of ceramics has extended far beyond the artistic domain.

A great variety of ceramic products are used in all the branches of engineering, and have to stand very severe conditions of service. They must perform with reliability at the limits of their possibilities. As a consequence the tendency is to impose very strict specifications on the ceramic material, as has been done with metals for many years. This condition has forced the ceramic industry to change progressively from an almost empirical technique to a scientifically controlled fabrication. The problems with which the ceramic engineer is faced are complex and greatly varied. The application of both physics and chemistry in the fabrication and in the use of ceramic products is so extensive that it seems strange no greater attention has been paid to it by scientists. In the following discussion an attempt will be made to describe a few typical problems in which the scientific approach has already given the ceramist a clear and accurate picture of the phenomena involved in industrial processes.

CONSTITUTION OF CLAYS

Clay being the most important raw material used in the fabrication of ceramic objects, an exact knowledge of its constitution and properties presents a very important problem. Until X-ray diffraction methods were ap-

plied to this problem, the nature of the structure of a clay particle was based mainly on hypothetical considerations. The microscopic method, so successful for the identification of crystalline components of rocks, did not give any definite information on the crystalline structure of clays because of the extremely small size of the particles. But more recently the X-ray diffraction method was systematically applied to clays by W. L. Bragg and L. Pauling, and the results of their studies not only showed the exact crystal structure of different clays, but also gave the clue to a logical explanation of some of their most important properties, and in particular their plasticity.

The crystal structure of clay is very complex, and it would be beyond the scope of this article even to try to give an account of the work which has been done in this field. However, it is possible to present a rather intuitive picture of the nature of the clay crystal, how it differs from other crystalline rocks and why it possesses such characteristic properties as plasticity. In a crystal of clay, as in any other crystal, the atoms are arranged in a definite pattern, forming a lattice. The special feature in a clay crystal is that the lattice is built of sheets of atoms. The crystal can be represented by a succession of parallel planes, the atoms being regularly arranged in each plane with the successive planes piled one on top of another.

The structure of kaolinite ($2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) will be described here as a typical example. It has been shown that unlike metals, such crystals as kaolinite are composed of ions and not atoms, and also that the hydrogen is always combined with oxygen to form a single ion

called hydroxile (OH^-). The different ions composing the kaolinite crystal are, therefore, Al^{+++} , Si^{+++} , O^- , and OH^- .

Before explaining the structure of kaolinite it is useful to consider two crystalline elements called hydrated silica and gibbsite. The hydrated silica is formed of three superimposed layers of hydroxile, silicon, and oxygen, respectively. A top view of these three layers is shown in *Fig. No. 1*, in which the ions are represented as spheres whose diameter is proportional to that of the ion. The bottom layer consists of oxygen ions arranged in a hexagonal plane lattice. On top of this layer is a layer of silicon ions forming also a hexagonal pattern. Since the diameter of the silicon ions is much smaller than that of the oxygen, the silicon ions fit into the space between three joined oxygen ions. The third layer is made of hydroxile ions placed just on top of each silicon of the middle layer. The diameter of the hydroxile is large enough so that the sphere representing these ions rests on the three oxygens of the bottom layer and the silicon is closely packed between four surrounding ions. It can be readily seen that the valences of each ion are saturated. Each silicon exchanges its four valences with three oxygen ions and one hydroxile. Each oxygen is saturated by two silicon, with which it is in contact, and one hydroxile exchanges its only charge with a silicon ion.

The second crystalline element entering the composition of clays is the gibbsite ($\text{Al}(\text{OH})_3$). It consists of three superimposed layers; namely, hydroxile, aluminum ion, and hydroxile. The bottom layer of hydroxile forms a closely packed hexagonal arrangement, as shown in *Fig. No. 2*. The aluminum ions constitute the second layer and are distributed in a hexagonal lattice. The top layer of hydroxile is closely packed like the bottom layer but displaced in such a manner that each hydroxile rests on three hydroxiles of the bottom layer. As in the case of the silicon in the hydrated silica, the aluminum ion is small enough to fit in the center of six closely packed hydroxiles.

The clay known as halloysite is obtained by stacking the three layers forming the gibbsite on to the three layers of hydrated silica. This results in six successive layers—oxygen, silicon, hydroxile, hydroxile, aluminum,

hydroxile. The reason for the bond which exists between the two middle layers of hydroxiles (one from the gibbsite and the other from the hydrated silica) is not quite clear because they lack any unsaturated valence. The forces involved in this kind of bond would seem to be due to the interaction between the electrical fields emanating from the two layers.

The crystal structure of kaolinite is very easily obtained from that of halloysite. The two middle layers of hydroxiles are combined into one single layer. When the consolidation occurs, the hydroxile ions combine in such a way as to form molecules of water, which are expelled. This process leaves a layer consisting of hydroxiles and oxygen. The kaolinite structure is, therefore, composed of five layers of ions in the following order: oxygen, silicon, hydroxile and oxygen, aluminum, and hydroxile.

The structural formula of a clay of the pyrophyllite type is also obtained by putting together the structure of hydrated silica and gibbsite. But in this case the gibbsite is inserted between two layers of hydrated silica, accompanied by a contraction and expulsion of water.

These structural formulas are easier to visualize when they are written with certain coefficients which give for each layer the number of atoms corresponding to six hydroxiles in the gibbsite structure. The two fundamental elements, hydrated silica and gibbsite, and the three typical kinds of clays may be represented as shown in Table No. 1.

In a particle of clay, a great number of these crystalline units are piled on each other. More than 100,000 of these units are necessary to obtain a clay particle 1/10000 of a millimeter in thickness.

THE PLASTICITY OF CLAYS

Numerous interpretations have been proposed to explain the plasticity of clays. Most of these interpretations have ascribed the plasticity of clay to the extremely small size of the particles. On this basis small particles adsorb a film of water which acts as a slipping surface between particles without decreasing the cohesive forces. Hence, a plastic clay would be regarded as an aggregate of rigid spheres of non-plastic material coated with a film of lubricant of suitable thickness. Such a simple

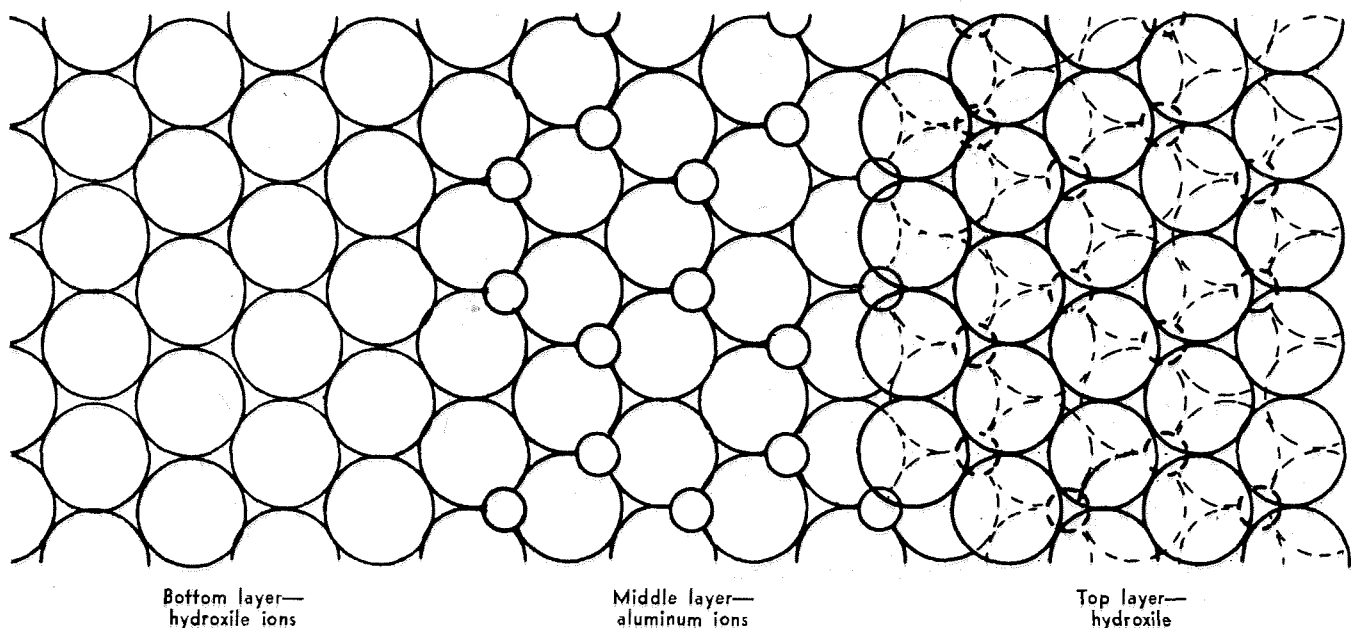
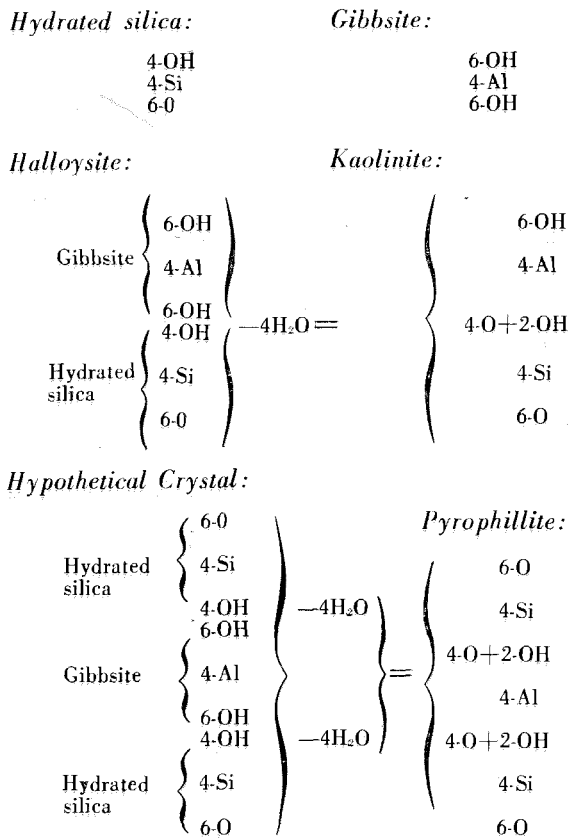


FIG. 2—Crystal structure of Gibbsite.

TABLE NO. 1



the crystal lattice. The plasticity may therefore decrease after the clay has been thoroughly dried. The plasticity is completely destroyed when the clay is fired at a sufficiently high temperature (above 550°C). Above this temperature the absorbed water is completely expelled and the hydroxile layers also produce water molecules which are removed. As a consequence, the entire crystal lattice collapses. The exact nature of the product resulting from this decomposition of a clay is not known. It is definitely established now that the product of decomposition does not give any X-ray diffraction pattern and therefore does not possess any definite crystalline structure.

The structural composition of kaolinite after being fired at a temperature above 925° C. is well known. It consists of crystals of mullite (3Al₂O₃.2SiO₂) and free silica. The latter may be present as amorphous silica, quartz, tridymite or cristoballite. The occurrence of one or several of these forms of silica depends primarily on the nature of the clay. The most suitable experimental method of studying the crystalline forms of silica in fired clay is by means of a dilatometer. Each form of silica undergoes allotropic transformations at certain temperatures. The temperatures of these transformations are different for different materials. These allotropic transformations are accompanied by an expansion.

As an example, the study of the structure of silica in four clays of different origin by dilatometric methods will be briefly described. The results to be discussed were obtained by means of a photo-recording dilatometer, for which the specimens consisted of small bars two inches long with a square cross section 3/32 inch by 3/32 inch. The specimens were cut from a block of fired clay by means of a thin diamond saw. The expansion-temperature curve was obtained with a rate of in-

concept of the mechanism of plasticity does not explain why a clay particle possesses an affinity for water, and does not explain why other materials like quartz or feldspar of particle size comparable to that of clay do not exhibit any appreciable plasticity when mixed with water.

The knowledge of the crystal structure of clay leads to a more satisfactory explanation of plasticity. It has been shown that water molecules can be absorbed by the crystal. These molecules form supplementary layers between adjacent crystalline units. These layers reduce the cohesive forces and thus provide planes for easy slip by which plastic deformation may occur. Some of the plasticity of clay may also be attributed to the adsorption of water molecules at the surface of the particles. This adsorption is due to the attraction between the outside layer of hydroxiles in a crystal of clay and the water molecules. The crystal of clay is, therefore, surrounded by a film of water as it was supposed in the older hypothesis, but the nature of the bond between the adsorbed water and the clay particle is connected with the crystal structure of the clay. It is then easy to explain why the water adsorbed by very small particles like quartz, for example, will not have the same plasticizing action as when adsorbed by a clay particle. Thus there are two different mechanisms by which plasticity in clays is obtained: namely, absorption of layers of water molecules in the crystal of clay, generating slip planes; and adsorption of a bonded film of water by the particles of clay, producing slipping surfaces.

FIRING OF CLAYS

Many features in the process of drying and firing clays can be explained by reference to their crystal structure. In the drying process, for example, it is rather difficult to expel the absorbed water without partially destroying

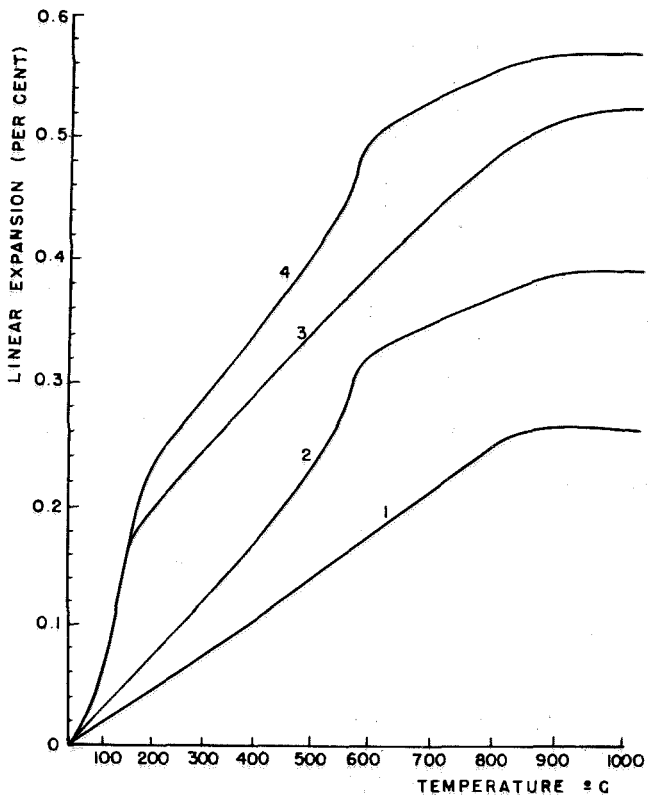


FIG. 3—Thermal expansion versus temperature for four clays of different origin, fired for six hours at 1350 degrees F.

crease of temperature of about $2^{\circ} C.$ per minute. This slow increase in temperature and the fact that the specimen was of small dimensions resulted in a very small temperature gradient in the specimen, and the allotropic changes took place in a minimum time. Four clays of approximately the same chemical composition but of different origin were fired for six hours at a temperature of $1350^{\circ} C.$ The four expansion curves are shown in *Fig. No. 3*. Clay No. 1 gave a straight line up to a temperature of about $850^{\circ} C.$, showing that no crystalline silica was present. This clay after firing consists of an aggregate of mullite crystals in a silica glass matrix. In clay No. 2 the presence of quartz is clearly shown by the sudden increase of expansion at $575^{\circ} C.$ In clay No. 3 the change in expansion coefficient takes place around $130^{\circ} C.$, indicating the presence of tridymite. The expansion curve of clay No. 4 shows definitely the presence of both quartz and tridymite. All these conclusions were checked by means of X-ray diffraction spectra, which revealed the presence of the constituents indicated by the expansion curves.

This typical example demonstrates the influence of silica on the average coefficient of expansion of a ceramic body. This average coefficient of expansion is of great practical importance in problems concerned with glazes in porcelain and china ware and also in the making of refractory bricks intended to resist thermal shock.

PROGRESS

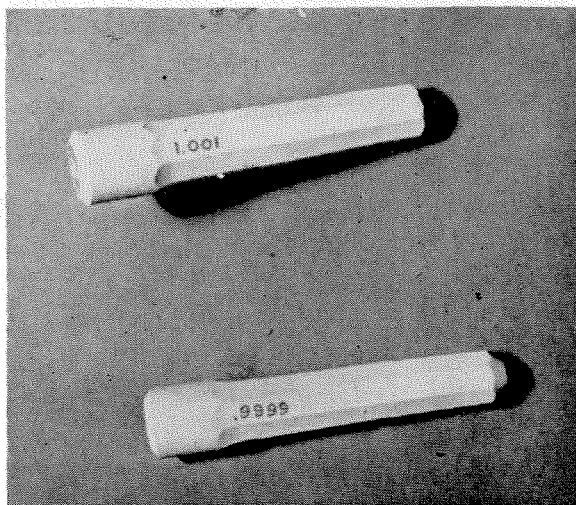
The demands of metallurgy for better refractory materials have been largely responsible for the progress made in the manufacture of refractories. This progress has resulted in a better control of the materials and in the development of new products. Simultaneously, methods have been developed for testing refractory materials under conditions approaching those found in service. Some of these tests, such as the determination of the softening point, the measurement of the load-bearing capacity at high temperature, and the spalling resistance of firebrick, have already been standardized. Other useful measurements, such as the thermal expansion, and the thermal and electrical conductivity, require more elaborate equipment, which is limited to very few laboratories. The resistance of a refractory to erosion and corrosion by a molten slag is of the greatest importance to the metallurgist. Laboratory tests reproducing the service conditions have already demonstrated their value.

Experimental research in ceramics is primarily dependent upon furnaces in which high temperatures can be easily reached with any desired atmosphere. Considerable progress has been made in this direction during the last decade. This achievement, together with the use of the methods of investigation which modern physics has placed at the disposal of the engineer, will greatly contribute to the development of research in the field of ceramics.

CERAMIC GAUGES

By B. W. MORANT

CHANGING conditions of the world have always brought about many new ideas in connection with production and the use of materials. One idea that has turned into a reality is the ceramic type of gauge, the earliest development of which occurred through the use of glass. Chief concern in any volume production program is the life of the tool before it must be taken out of service for replacement or reconditioning. The next concern is how cheaply and how quickly it may be replaced. The ceramic gauge offers a valuable solution for



Ceramic gauge, designed to replace gauges of critical metals.

both of these problems as it is very resistant to wear, and is quickly and cheaply produced and replaced.

While there are many reasons for substituting non-critical materials for those in the more critical classifications, it is unnecessary to analyze the ceramic gauge for anything but its own direct merits. At all times the raw material from which it is made is both plentiful and cheap. The product is very hard and of excellent wearing quality. The rough blank is easily produced by pressure with the minimum of equipment. By varying their composition, ceramic gauges may be provided with a wide range of coefficients of expansion. Oxidation of ceramic gauges does not present any problem, and perspiration does not etch their surfaces. Ceramic gauges do not tend to gall when used with copper alloys. Compressive strength of ceramic gauges can be as high as 100,000 pounds per square inch. Tensile strength, however, will vary from 5,000 pounds to 15,000 pounds per square inch. Similarly the impact strength of ceramic materials is low.

At first glance these last factors discourage industry from the general use of ceramic gauges. However, experts with steel gauges agree that after a gauge has been dropped, it should not be relied upon until standardized. The ceramic gauge is never in doubt because it always dismembers itself or else is picked up in an immediately usable condition. The behavior of ceramics is such that an impact which is sufficient to remove a small chip does not affect the balance of the dimensional characteristics, although intraconchoidal fracture may result on the second or third impact. Therefore, in order to prevent or at least minimize breakage from rough handling, the ceramic gauge should have all exposed edges beveled or finished to a radius.

Briefly, the blank for a ceramic gauge of the type so far considered is slip cast, hollow, and with or without integral handle. It is provided with cast-in-center bores at each end to facilitate the finish grinding. The blank is capable of great accuracy as cast and fired, but the usual finish grinding operations are required to meet the tolerances demanded.

In the above comments an attempt has been made to present some of the factors involved in the use of ceramic gauges, both favorable and unfavorable, in order that the reader may draw his own conclusions as to why after more than a year of general consideration and in

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