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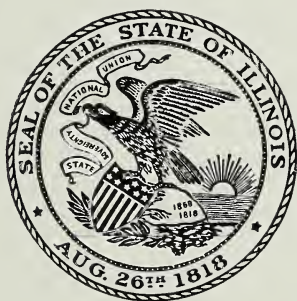STATE GEOLOGICAL SURVEY
M. M. LEIGHTON, *Chief*
URBANA

(1)   Elements of the Petrographic Study of Bonding Clays
and of the Clay Substance of Molding Sands

RALPH E. GRIM

(2)   Mineral Composition and Texture of Clay Substance
of Natural Molding Sands

RALPH E. GRIM AND CARL E. SCHUBERT

(3)   The Relationship Between the Physical and Mineralogical
Characteristics of Bonding Clays

RALPH E. GRIM AND RICHARDS A. ROWLAND

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CONTENTS

ELEMENTS OF THE PETROGRAPHIC STUDY OF BONDING CLAYS AND OF THE CLAY SUBSTANCE OF MOLDING SANDS*

By Ralph E. Grim

ABSTRACT

This paper briefly outlines the modern methods for the study of clay materials, the prevailing concept of the composition of clays, and the application of modern clay researches to studies of natural molding sands and bonding clays. An appended bibliography of a selected list of reports giving details and theoretical considerations of points discussed is included.

INTRODUCTION

It has been known for a long time that molding sands are essentially mixtures of silica sand and clay substance with more or less yellow or red hydrated ferric iron oxide. This fact is recognized in the preparation of synthetic sands by mixing silica sand and bonding clay.

Papers[1] have been published in the A.F.A. Transactions describing in detail the characteristics of the silica: shape of grains, grain size distribution, etc. Detailed information on the clay substance has not been obtained and investigations of molding sands state only that the quality of the clay substance varies in different sands without making any attempt to study it in detail. Some reports give chemical analyses of the clay, but it is generally recognized that chemical data alone tell very little about the character of a clay.

Within the last ten years a large amount of work has been done on the development of methods for the study of clays and in actually studying them by these new methods. A large number of publications in many scientific journals have reported new and important data on the composition and properties of clay materials. As a consequence of this recent work, the characteristics of the clay substance of a molding sand can now be determined as thoroughly as the characteristics of the silica sand portion.

It is proposed in the present paper to briefly outline the modern methods for the study of clay materials, to state the prevailing concept of the composition of clays, and to point out the application of modern clay researches to studies of natural molding sands and bonding clays. For details and theoretical considerations of any points considered herein, reference should be made to the reports of the work on which this paper is based. The appended bibliography is a selected list of such reports.

CLAY COMPOSITION

If a pure clay[2] could be examined with a microscope magnifying many thousand times, it would be found that it was nothing but an aggregation of flake shaped particles. The actual size of these flakes would vary from several microns[3] to less than 0.1 micron in diameter. A working picture of the makeup of clays may be had if one starts with large flakes of mica and then reduces the size of the flakes until each flake is about one micron in size. A mass composed of such flakes approximates the makeup of a clay. If the flakes composing clays are analyzed, it is found that they are composed of atoms of aluminum, silicon, oxygen, and hydrogen. Potassium, magnesium, and/or iron would be found in the flakes of some clays.

[1]Ries, H., and Conant, G. D., The character of sand grains: Trans. Am. Foundrymen's Assoc., Vol. 39. pp. 353-392, 1931.

Ries, H., and Lee, H. V., Relation between shape of grain and strength of sand: Trans. Am. Foundrymen's Assoc., Vol. 39, pp. 857-860, 1931.

Note: This paper was presented at the Sand Research session of the 43rd annual A.F.A. Convention, Cincinnati, O., May 17, 1939.

[2]The discussion of clay composition holds for almost all clays. There may be, however, a few relatively unimportant clay materials which have a composition slightly different from that presented.

[3]One micron is one thousandth of a millimeter (0.001 mm.) or about one twenty-five thousandth of an inch (0.00004 in.).

The atoms have a definite arrangement in the flakes; e.g., the silicon atoms have fixed positions with respect to the oxygen atoms, the aluminum atoms have definite positions with respect to the oxygen atoms, and so on for the other elements. Substances composed of atoms arranged in a definite pattern are crystalline, and hence the flakes which compose clays are crystalline. The flakes are minute fragments of crystals.

That fraction of clay composed of particles smaller than a given size (± 1 micron) is the so-called colloid fraction. The colloidal material in clay is made up of crystalline clay mineral flakes, and it is not an amorphous heterogeneous mixture of silica, alumina, etc.

There are several important kinds of flakes which make up clays. All the different kinds of flakes are composed of about the same atoms, but for each kind of flake there is a distinctive and different arrangement of the atoms. From the viewpoint of mineralogy, the different kinds of flakes are different mineral species and warrant different mineral names. These minerals, which are the essential constituents of clays, are called clay minerals. Extensive analysis of clays has shown that there are only three important clay minerals, and that almost all clays are composed essentially of extremely minute flake-shaped particles of one or more of these three minerals (Table 1). In addition to the clay minerals, minor amounts of quartz, organic material, limonite, and other minerals, are also found in many clays. Some examples of the composition of clay materials are as follows: Bentonites are made up of extremely minute flakes of montmorillonite, shales are composed usually of particles of illite frequently with quartz and other minor constituents, fireclays are usually mixtures of flakes of kaolinite and illite, and kaolins and china clays are made up essentially of particles of kaolinite.

TABLE 1.—Important Clay Minerals

Name	Chemical Composition
Kaolinite	$(OH)_8Al_4Si_4O_{10}$
Illite	$(OH)_4K_y (Al_4 \cdot Fe_4 \cdot Mg_4 \cdot Mg_6)$ $(Si_{8-y} \cdot Al_y) O_{20}$
Montmorillonite	$(OH)_4Al_4Si_8O_{20} \cdot XH_2O$

Since the atoms are arranged differently in the three important species of clay minerals, it follows that their characteristics, and the physical properties of the clay which they make up will be different; e.g., the characteristics of kaolinite will be unlike those of montmorillonite and the physical properties of a clay composed of kaolinite will be different from those of a clay composed of montmorillonite.

CLAY MINERAL PROPERTIES

In the following discussion some of the characteristics of the three important clay minerals which are related to the properties of natural molding sands and bonding clays are considered.

The montmorillonite clay minerals usually occur in particles less than 1 to 0.1 micron in diameter, or in larger particles which are easily reduced to this size when the clay is worked with water. Kaolinite occurs in particles which are rarely smaller than 1 micron and which are not easily broken down by working in water. Most illite occurs in particles about the same size as kaolinite, but there are some clays in which the illite flakes are much smaller. It follows, therefore, that if a clay composed of montmorillonite is compared with one composed of kaolinite, the montmorillonite clay will be made up of smaller flakes than the kaolinite clay. As a consequence, a given amount of montmorillonite clay will contain a larger number of flakes, and a larger total flake surface than will a kaolinite clay. As many of the properties of clays are closely related to the size of their component particles, it follows that this difference between montmorillonite and kaolinite would cause clays composed of montmorillonite to have properties that differ from those composed of kaolinite.

All the clay minerals have the power to adsorb certain ions. Thus, if a solution containing lime is passed through a clay some of the lime will be taken out of solution by the clay unless the clay already has all the lime it can adsorb or the lime solution is too dilute. The adsorbed ions are exchangeable, e.g., if a clay carrying lime is treated with a potash solution, some of the adsorbed lime will be replaced by potassium ions. Hydrogen, sodium, potassium, calcium, and magnesium are the common exchangeable ions held by clays. Montmorillonite has about ten times as much capacity as kaolinite to hold adsorbed ions. The capacity of illite varies; some illite has the capacity of kaolin-

ite, whereas other illite has several times this capacity. The difference in the adsorptive capacity of clay minerals is illustrated by their dye adsorption; a montmorillonite clay will adsorb much more dye than a kaolinite clay.

It is known in a general way that the physical properties of clays vary with the ion which the clay carries. An example will illustrate the point; if the green and dry compression strengths of two montmorillonite clays are compared, one of which carries hydrogen and the other sodium as the exchangeable ion, it will be found that the hydrogen clay has higher green strength than the sodium clay, and that the hydrogen clay has lower dry strength than the sodium clay. The exact variation of bonding properties caused by various exchangeable ions is a promising field of future research which remains to be worked out.

The clay minerals differ from each other in their refractoriness and in their dehydration characteristics. Kaolinite fuses at a much higher temperature than either montmorillonite or illite. Kaolinite loses all of its water when it is heated to about 900°F., and after subjection to this temperature does not again regain its moisture or its physical properties when cooled to ordinary temperatures. Montmorillonite may be heated to about 1025°F. before its moisture is permanently removed and its physical properties are destroyed. The dehydration characteristics of illite are not well known. The above temperatures are equilibrium temperatures. Montmorillonite, for example, must be held at 1025°F. for a considerable period of time before it is completely changed. When montmorillonite is heated to 1025°F. and immediately cooled, only a small amount of it is irreversibly dehydrated.

It is clear from the foregoing considerations that clays composed of different clay minerals must have different properties. A large amount of work must be done before the relation between the various clay minerals and bonding properties are well understood, but some information on this subject is available. It is known, for example, that montmorillonite clays have higher compression strengths than kaolinite clays, and that some illite clays are weak, whereas others have high strength. Thus, a mixture of 95 per cent sand and 5 per cent clay composed of montmorillonite will have greater green

and dry strengths than a mixture of 95 per cent sand and 5 per cent kaolinite clay at their optimum moistures. The properties of bonding clays depend, therefore, on the clay minerals of which they are composed. Also, as brought out before, the properties will vary depending on the exchangeable ions which they contain.

Similarly, it is clear that two natural molding sands with the same fineness characteristics, and the same amount of clay will not necessarily have the same strength. In fact the natural sands can *not* have the same strength unless their clay is made up of the same clay mineral carrying the same exchangeable base. It is obvious, then, that the properties of two sands cannot well be compared without information on the character of their clay mineral content.

DETERMINATION OF MINERAL COMPOSITION

It is easy to study the characteristics of the sand grains and of the coarse silt in molding sands with the microscope. Clays generally or the clay substance of molding sands cannot be studied so easily because they are composed of particles which are so small that they cannot readily be seen with the microscope even using very high magnification, much less identified and studied. These very small particles are mostly the clay mineral flakes just mentioned, and only lately has it been possible to devise techniques for their adequate study. In the following paragraphs these techniques are reviewed briefly.

X-ray Method

When a beam of x-rays is passed through a crystalline substance, the beam is reflected and refracted from the planes of atoms which make up the crystal. The x-rays emerge from the crystal as a series of beams which can be recorded on a photographic film as a series of lines (fig. 1) or dots, depending on the details of the procedure followed and the character of the material. The position, intensity, and number of beams emerging from any crystalline substance depend on the character of its atoms and their arrangement in the substance. Thus, it follows that if two crystalline substances with different atomic structures are placed in front of x-ray beams and the
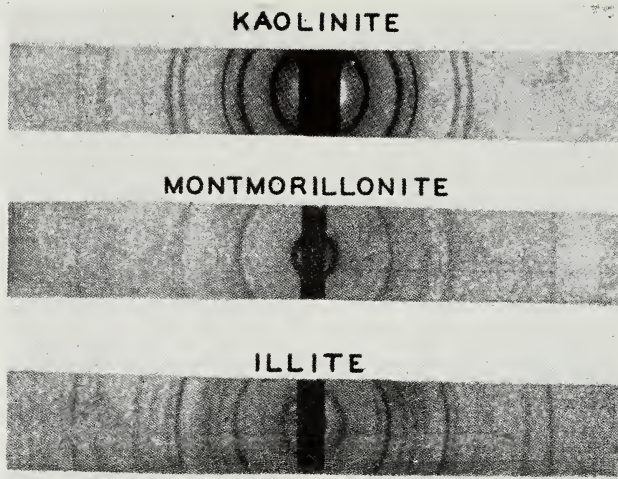
Fig. 1—X-ray Diffraction Patterns. (After W. Noll., Ber. Deut. Keram. Ges. 19, p. 181, 1938)

emerging beams are recorded on photographic films, the pattern of the lines on the films will be different.

The clay minerals have different atomic structures and, therefore, yield different x-ray patterns. Thus, if a beam of x-rays is sent through a clay sample and the emerging beams recorded, it is possible to determine from the recorded beams the minerals which make up the clay, regardless of the fact that the particles composing the clay are extremely small. The identification of the minerals is made by comparing the pattern from the clay with patterns of known pure mineral material.

One of the greatest difficulties in the identification of the constituents of clays has been to obtain pure samples of many of the minerals found in clay for determining standard analytical data. Thus, it is difficult to obtain pure illite for the study of its x-ray, optical, chemical, and other properties which can be used as a basis of comparison and hence for the identification of illite in clays generally.

It is frequently possible to work out the exact arrangement of the atoms within a crystal from the pattern of the emerging beams of x-rays. In recent years a large body of data has become available on the arrangement of the atoms within the various clay minerals. This work is providing, perhaps for the first time, a fundamental, basic explanation of the physical properties of clays.

MICROSCOPIC METHOD

One difference between crystalline and noncrystalline substances is that in crystals the velocity of light traveling through them depends on the direction of the path of light. In a flake of mica for example, light passing through the flake at right angles to the flake surface has a different velocity than light passing through parallel to the flake. Another character of crystalline material is that light passing through it is polarized, i.e., broken up into light vibrating in only one plane. As a result of these phenomena crystalline substances have certain optical properties. The optical properties of crystals are dependent on their atomic structure and, therefore, materials with different crystal structures, such as the clay minerals, have different optical properties. The petrographic microscope is constructed so that optical properties can be measured and, as a consequence, minerals can be identified. Satisfactory determinations, however, can only be made on individual particles coarser than about 1 micron, which is larger than many of the clay mineral particles in clays. This limitation to the application of petrographic microscopic technique in the study of clays has been overcome by taking advantage of the flake shape of the clay mineral particles. Aggregates of clay minerals can be prepared in such a way that the flakes rest on top of each other in the same relative crystallographic position. The optical properties of the aggregates can be measured as if they
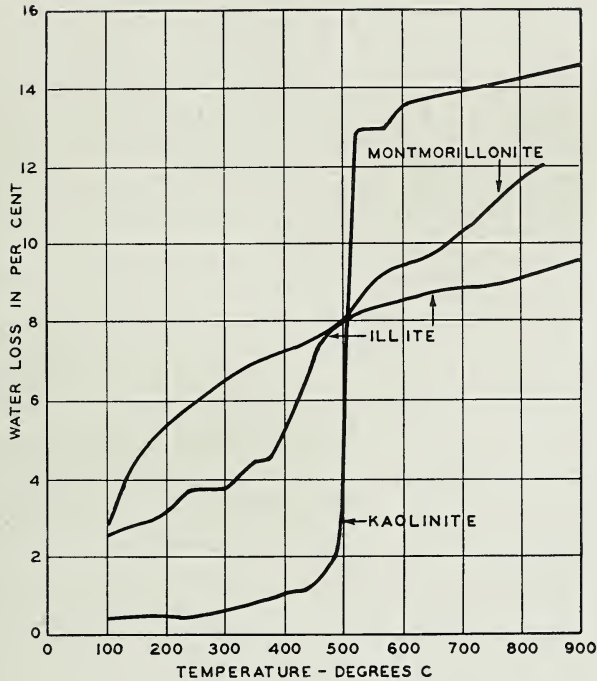
Fig. 2—Dehydration Curves

were large individual crystals. In this way the component particles can be identified even though they are too small to be seen individually. The aggregates are prepared by carefully drying suspensions of the clay.

Dehydration Method

The clay minerals contain different amounts of water, and they lose their water at different temperatures when heated (fig. 2). Thus, it would seem possible to determine which clay minerals are present in a clay by determining the amount of water present and the loss of water as the clay is heated. The method has been used in clay studies, but it must be used with caution chiefly because the dehydration characteristics of the clay minerals vary with the size of the particles in which they occur. It has been shown, for example, that extremely finely ground mica has dehydration properties that differ from those of the same mica composed of coarser particles.

Chemical Method

Past studies of clay materials have frequently included chemical analyses. In general, chemical analyses alone do not permit an identification of the mineral components of clay substances. Such determinations give values for the amount of silica, alumina, etc., in the substance but do not indicate in what minerals they are present. Therefore, the chemical data do not give information on the units making up the clay which largely determine its properties, i.e., the clay minerals. Along with x-ray and optical analyses, chemical data are helpful; alone they have little value.

Application of Present Methods

The study of clay materials has shown that they are frequently composed of mixtures of clay minerals. Clay minerals occurring in mixtures are particularly difficult to study and identify because, although the optical and x-ray properties of the clay minerals on which identification is based are different, the differences are not great and frequently the analytical data for mixtures cannot be interpreted readily. For example, x-ray and optical analytical data for a clay composed of a large proportion of one clay mineral, and a minor amount of another clay mineral, may not positively indicate the presence of the minor component. To overcome this difficulty, a fractionation proced-

ure has been developed which literally takes the clay apart into fractions of its component minerals. The object is to isolate the clay minerals in fractions of sufficient purity so that they can be identified positively.

The general procedure is as follows: The material is disaggregated and placed in suspension in water, using ammonia as the dispersing agent. The suspension is allowed to stand until the material coarser than 2 microns has settled out. The suspension carrying the -2 micron particles then is removed and saved, and the settled material again is placed in suspension and allowed to stand until particles coarser than 2 microns have settled. This process is repeated until the material coarser than 2 microns has been freed of particles smaller than this size, i.e., the sample has been split into a fraction carrying $+2$ micron particles and a suspension carrying finer particles. The particles in the coarse fraction can be identified and studied individually by means of the petrographic microscope.

Oriented aggregates are prepared of the material in the suspension and they are studied with the petrographic microscope. If the finest fraction of the clay is composed of only one clay mineral, it can be studied adequately by x-ray and optical analyses of the entire -2 micron grade size. If the finest grade size is a mixture of clay minerals, it may be necessary to fractionate the suspension by sedimentation (e.g., pipette analysis) or by supercentrifuge processes. By running the suspension through a super-centrifuge, it is possible to separate the particles of the suspension into size fractions. Frequently, fractions containing particles 2 to 1 microns, 1 to 0.1 micron, and -0.1 micron are obtained. Because the clay minerals tend to break down into different sizes, a concentration of clay minerals will be effected by such a fractionation. For example, if the suspension contained kaolinite and montmorillonite, the kaolinite would tend to be concentrated in the $+1$ micron fraction and the montmorillonite would be concentreted in the -1 micron fractions. Fractions of relatively pure clay minerals would be obtained which would permit accurate identification of the constituents of the clay.

Thus by taking a clay material apart a complete picture of its makeup can be obtained. Also the technique gives some information on the size distribution of the min-

erals making up the material. Such data on the makeup of clays and molding sands are the fundamentals on which studies of the causes of variation in properties must be based. They are the necessary starting point for investigations of why molding sands and bonding clays have the properties they do, and what determines their variations. Until the factors controlling the properties of sands are understood, the sands themselves cannot be controlled with complete satisfaction.

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DISCUSSION

Presiding: H. S. WASHBURN, Plainville Casting Co., Plainville, Conn.

DR. H. RIES[1]: We all realize that this subject is a very deep one and it may seem intensely theoretical, but I believe it brings out one very important point, and that is that as we go farther with the study and the research on molding sands, that we are getting down into finer and finer details. I presume when we first started on molding sands back in 1921, at a time when I think all of us will admit now we did not know anything about them—we thought we did, but we have found out since how little we actually did know—we did not think of these very small details. We knew, of course, that sands had bonds and that these bonds behaved in different ways. Now, we are coming to a point where we are beginning to study these bonds in greater detail. Of course, the study of them requires a considerable expertness, particularly when you have to use these high-powered, complicated microscopes, but, as Dr. Grim has pointed out, we do have these different clay minerals in the bond, and it has been shown that they have different bonding properties, and so that would tend to explain why certain clays might be more efficient as bonds than others.

But there is another interesting point which I think he has brought out—I am not sure whether he mentioned these by name—namely base changes, the possibility of kicking out one ion in a clay and substituting another ion for it, as, for instance, the comparison he drew in the case of this water softening material, the zeolites.

To put it in plain language, we might say we give the clay a dose of salts and, as a result of that, it behaves differently from what it did before.

That opens up an interesting field. It is possible that if a bonding clay does not behave just right, perhaps by treating it with some chemical and getting the ions of this chemical to take the place of certain ones which were in the clay, we may improve its properties. Of course, whether we do it or not may be influenced somewhat by the expense which might be incurred by doing so, but I think it is something that will be worth trying in the future.

[1] Cornell University, Ithaca, N. Y.

MEMBER: In the very descriptive information as to the constitution of these various layers, Mr. Grim pointed out that in certain clays the structure shows a contact point of, in one place OH and the other point, O. Does he by these terms indicate that there is actually atomic OH or atomic O? That is, is this contact point based on a chemical reaction?

DR. GRIM: The OH and the O are not in contact. They are parts of different units that tend to make up the whole lattice structure. The theory of the thing is that because you have the OH in the top layer of one kaolinite unit and O in the bottom layer of the next unit, there is a tendency to hold the units in a relatively fixed position which is more secure than you would have if O and O were in adjacent layers of two units (e.g. montmorillonite).

MEMBER: That supposedly is based on the affinity of those elements for each other?

DR. GRIM: Yes, that is the basis for it.

MEMBER: Dr. Grim could you show by a molecular diagram what happens when the clay substance loses its water? In other words, dehydration.

DR. GRIM: That depends on what sort of clay you are talking about. In the case of montmorillonite, the lattice structure seems to be retained in all of its attributes up to about 550°C. That is about 1025°F. There may be a considerable amount of water present in montmorillonite between the structural units but that is lost at relatively low temperatures, perhaps of the order of magnitude of 220 or 250°F. Above 550°C. the whole lattice tends to break down and different constituents are formed before eventual fusion. Exactly what the mineralogical changes are that take place when montmorillonite and illite break down, are not known, but it is quite well known for kaolinite because the ceramists have worked it out in their study of China clay. There is a change to cristobalite, which is a high temperature form of quartz, and mullite, which is aluminum silicate. As the temperature is raised above the temperature where all the water is lost, mullite and cristobalite form eventually and then later fusion takes place. To be perfectly correct, there is some dispute among ceramists as to the exact sequence of changes that take place within that range when all the water is gone and before the new crystalline material develops. It is difficult to get any positive evidence on which to identify the material. X-ray pictures provide patterns that are very difficult to interpret and you can not see much under the microscope.

MEMBER: Dr. Grim showed the difference between the adjacent layers of kaolinite as differing from montmorillonite and their apparent attraction for each other. What would be the case there in the instance of the illite as regards the adjacent oxygen atoms?

DR. GRIM: Illite differs from montmorillonite in that some of the silicon atoms are replaced by aluminum atoms in the silica tetrahedral sheet. In the lattice structure, silicon carries four charges and aluminum carries three. Every time a silicon is replaced by an aluminum, there is one excess charge in the lattice and that excess charge is usually compensated by an atom of potash that occurs on top of the silica sheet. The potash ions in between the silica sheets act as sort of a bridge that binds them together, so that they do not swell and come apart easily.

MINERAL COMPOSITION AND TEXTURE OF THE CLAY SUBSTANCE OF NATURAL MOLDING SANDS†

By Ralph E. Grim* and Carl E. Schubert**

ABSTRACT

The authors experimented with samples of eight different molding sands. Six of these sands are in commercial use and two are potential Illinois molding sands. The size-grade distribution of the clay substance is determined, the minerals making up the clay substance of each sand were identified, and the distribution of the important mineral constituents with respect to particle size was determined. Curves of the frequency distribution of the various samples are included.

INTRODUCTION

The clay substance of a molding sand is defined by the American Foundrymen's Association[1] as that part occurring in particles less than 0.02 mm. in diameter. The physical properties of any sand are closely related to the detailed characteristics of its clay substance[2] and, consequently, properties cannot be well understood until the clay substance has been studied in detail.

In the researches herein reported, the size-grade distribution of the clay substance was determined for each one of a number of molding sands selected because the general character of their clay was thought to vary. Also, the minerals which make up the clay substance of each molding sand were identified and the distribution of the important mineral constituents with respect to particle size was determined.

Objective

The objective of the present study was to obtain detailed analytical data for the clay substance of various natural molding sands and thereby to develop a basis for a study of the factors controlling some of the physical properties of natural sands.

Sands Investigated

The molding sands investigated are listed in Table 1, together with their content of clay substance and their green compression strength at optimum moisture. Six of the samples are molding sands in commercial use, and two samples are potential Illinois molding sands obtained by the Illinois Geological Survey in a recent study of the molding sand resources of Illinois.

PROCEDURE

The amount of clay substance was determined by the standard method of the American Foundrymen's Association.[1]

Table 1.—Clay Substance and Green Compression Strength of Molding Sands

Sample No.	Clay substance Per cent	Green compression at optimum moisture lb. per sq. in.
1	20.0	18.0
2	10.8	7.5
3	19.2	13.5
4	21.2	13.0
5	16.8	11.0
6	6.6	12.5
7	26.0	14.5
8	46.6	21.0

The size-grade distribution within the clay substance was determined on an aliquot of the original sample by pipette method, as applied to molding sands.[3]

[1]Testing and grading molding sands and clays: Am. Foundrymen's Assoc., 1938 edition, pp. 26-27, 157-158.
[2]Throughout this report "clay substance" is used as defined by the American Foundrymen's Association.
†Reprinted from Trans. Am. Foundrymen's Assoc., Vol. 47, No. 4, pp. 935-53, 1940.
*Petrographer, Illinois State Geological Survey.
**Associate in Mechanical Engineering, University of Illinois.
Note: This paper was presented before the Sand Research Session of the 43rd Annual A.F.A. Convention, Cincinnati, O., May 17, 1939.

[3]Jackson, C. E., and Saeger, C. M. Jr., Use of pipette in the fineness test of molding sands: U. S. Bur. Standards, Jour. of Research 14, 1935, pp. 59-66.

In order to obtain samples for mineralogical study, another aliquot of the original sample was dispersed in water using NH_4OH as the dispersing agent. The suspension was then allowed to stand until particles larger than 0.02 mm. had settled out. The suspension carrying -0.02 mm. material was then removed and allowed to stand until the $+0.01$ mm. particles had settled out. The particles settling out of this suspension ranged in size from 0.02 mm. to 0.01 mm. contaminated by some finer material. By repeatedly placing this settled material into suspension and removing the -0.01 mm. particles, a fraction containing only grains ranging from 0.02 mm. to 0.01 mm. was obtained. By a similar procedure, but with different settling times, fractions containing particles from 0.01 to 0.005 mm., 0.005 to 0.002 mm., -0.002 mm., and -0.001 mm. were obtained. NH_4OH was used as the dispersing agent, because on evaporation no salt is left as a residue.

The minerals making up the fractions coarser than 0.002 mm. were identified on the basis of their optical characteristics using the petrographic microscope. The components of the fractions finer than 0.002 mm. were identified on the basis of their optical and x-ray characteristics.

Determinations of green compression strength and fineness characteristics were made by the standard A. F. A. procedures.

PARTICLE SIZE ANALYSES

The results of the determinations of size-grade distribution were plotted in the form of cumulative curves on semi-logarithmic paper. From the cumulative curve of each sample, a frequency distribution curve (figs. 1A to 8A) was constructed by the graphic differentiation method described by Krumbein.[4] The frequency curves show the relative abundance of various size grades by the area under the curve. For example, the percentage of material between 0.005 and 0.002 mm. in any sample is obtained by dividing that portion of the area under the curve which is bounded by vertical lines constructed at the 0.005 and 0.002 mm. divisions of the horizontal axis by the total area under the curve; e.g., in figure 1A, 15 per cent of the total area under the curve lies between the 0.005 and 0.002 mm. verticals, and therefore 15 per cent of the sample occurs in the 0.005 to 0.002 mm. grade size. Thus the relative abundance of any size can easily be visualized or accurately determined.

The relative amount of -0.0005 mm. material is represented by the area of the rectogram thus,

$$\text{Per cent material—} \atop 0.0005 \text{ mm.} = \frac{\text{Area of rectogram}}{\text{Area beneath curve including area of rectogram}}$$

If the -0.0005 mm. fractions were presented as a continuation of the curve rather than as a rectogram, the curves would extend to infinity since the -0.0005 mm. fraction contains all material from 0.0005 mm. to an infinitely small particle size.

The chief components of the clay substance of the molding sands studied are quartz, clay minerals, and limonite.[5] The distribution and relative abundance of the quartz and clay minerals plus limonite are shown by figures 1B, C to 8B, C. The clay minerals and limonite are shown together because together they are chiefly responsible for the strength properties of the sand, and because they cannot well be separated in such material on an accurate quantitative basis.

In figures 1B, C to 8B, C the distribution curves of the entire clay substance are broken down into two curves representing, respectively, the distribution of quartz and the clay minerals plus limonite. The distribution curves for the total clay substance are constructed on the basis of weight analyses. The curves for the component mineral are constructed on the basis of numerical values. The shape and specific gravity of the particles are sufficiently alike so that the curves are comparable.

An analysis of figures 1A, B, C will illustrate the data contained in the curves. The area beneath the curve for the clay minerals plus limonite, added to the area beneath the curve for quartz is equal to the area beneath the curve for the total clay substance, and thus in the clay substance:

$$\text{Per cent} \atop \text{quartz} = \frac{\text{Area beneath quartz curve}}{\text{Area beneath curve for total clay substance}}$$

[4]Krumbein, W. C., Size frequency distribution of sediments: Jour. Sed. Petrology, vol. 4, 1934, pp. 65-77.

[5]Limonite is used throughout the report for the hydrated ferric iron oxide compounds present in the clay substance.

Fig. 1—Frequency Distribution Curves for Sample 1.

Fig. 2—Frequency Distribution Curves for Sample 2.

Fig. 3—Frequency Distribution Curves for Sample 3.

Fig. 4—Frequency Distribution Curves for Sample 4.

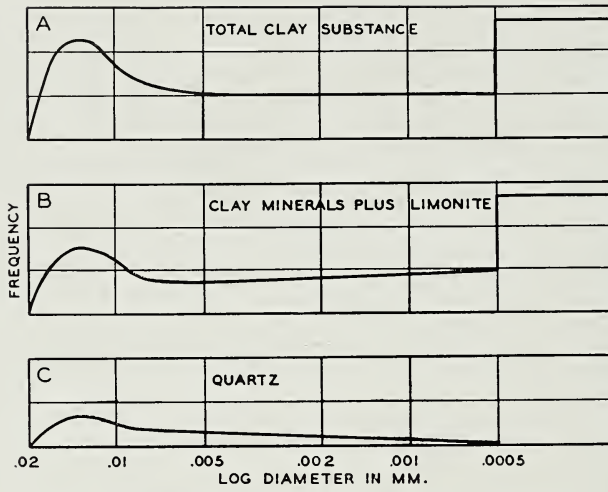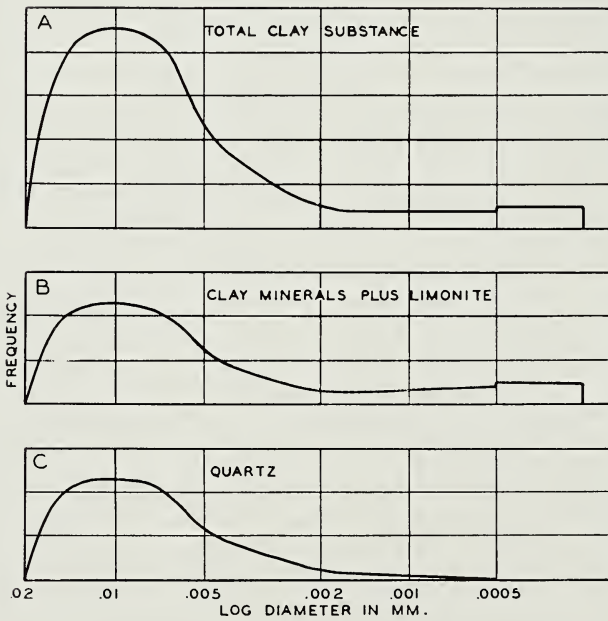Fig. 5—Frequency Distribution Curves for Sample 5.

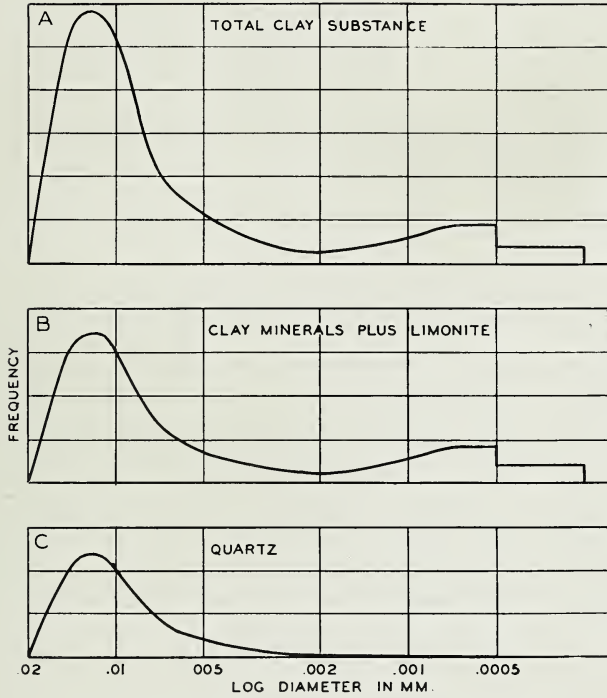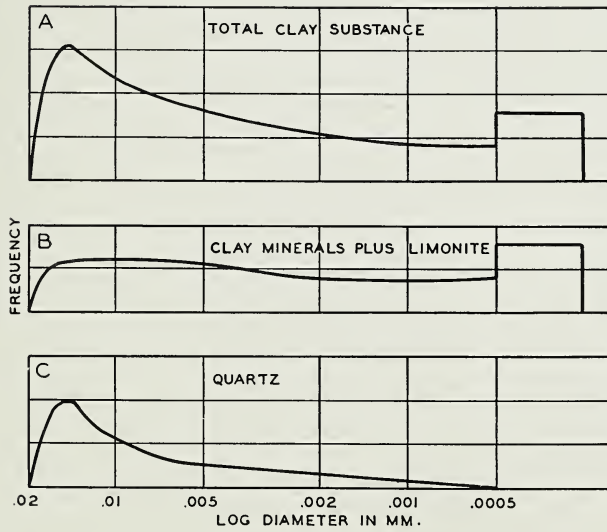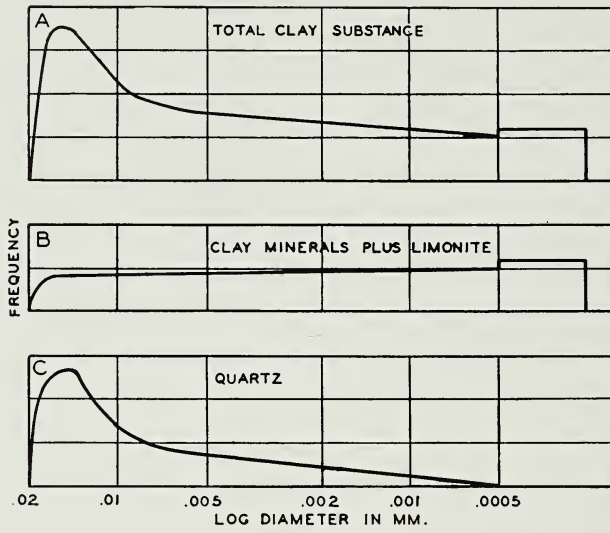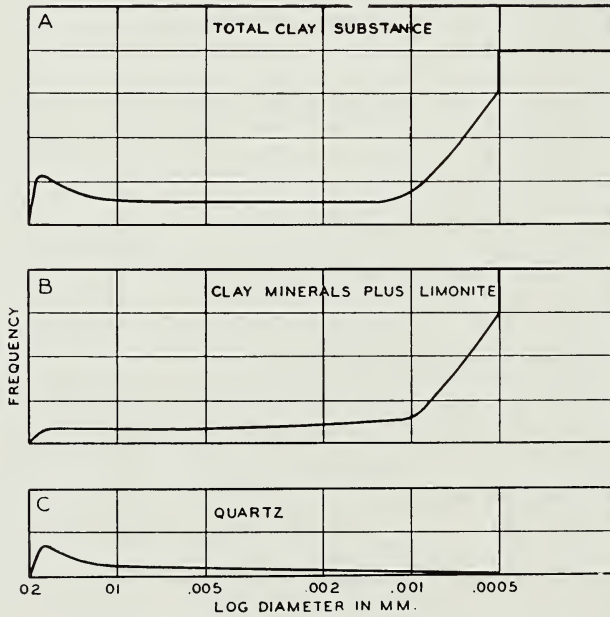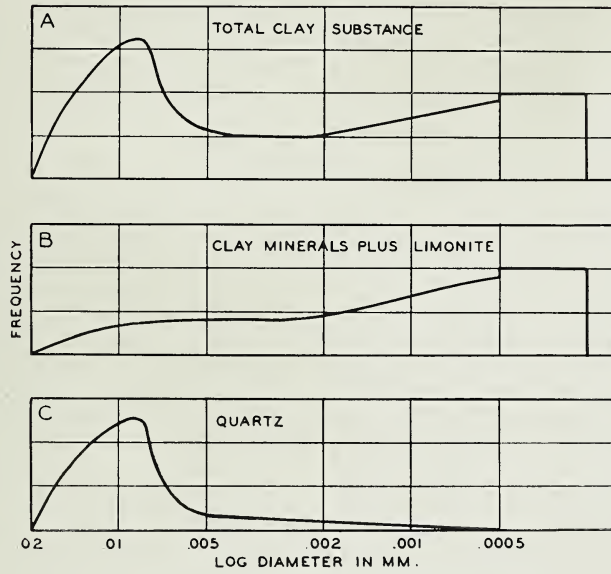
Fig. 6—Frequency Distribution Curves for Sample 6.

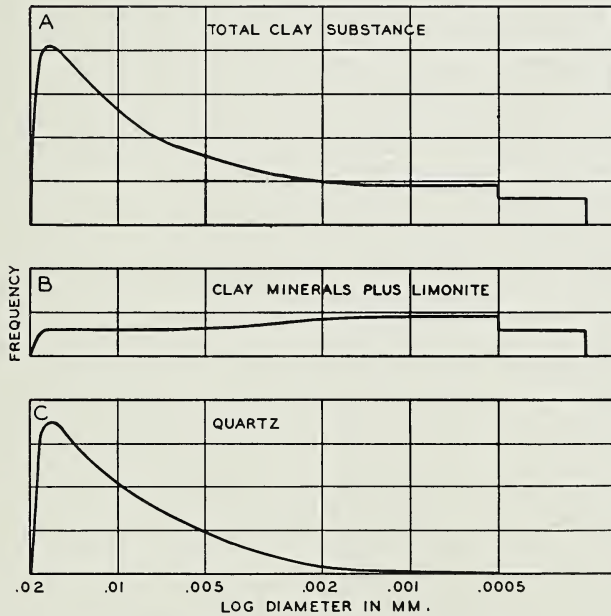Fig. 7—Frequency Distribution Curves for Sample 7.

Fig. 8—Frequency Distribution Curves for Sample 8.

The frequency curves for the quartz and clay minerals plus limonite represent the size-grade distribution of these constituents in the same manner that the curve for the entire clay substance represents the size-grade distribution of the entire clay substance. For example, in the curve for the clay minerals plus limonite (fig. 1B), the area under the curve and between vertical lines drawn at 0.02 and 0.01 mm. is 13 per cent of the total area under this curve, and therefore 13 per cent of the total clay minerals plus limonite occurs in the size grade 0.02 to 0.01 mm. The curves are so constructed that the area under curve B between any grade size, plus the area under curve C between the same grade size is equal to the area beneath curve A between these grade sizes. Thus, in figure 1 the area under curve B between 0.02 and 0.01 mm. is two thirds of the area under curve A between 0.02 and 0.01 mm., and therefore two thirds of the clay substance occurring between 0.02 and 0.01 mm. is clay mineral plus limonite. It is possible, therefore, from the above curves to determine the relative amount of the mineral components in the total clay substance and in any size grade.

ANALYTICAL RESULTS

The clay substance of sample 1 shows a concentration of material in the 0.02 to 0.01 mm. and the —0.0005 mm. grade sizes. Only a small proportion of the clay substance is quartz, and it is concentrated slightly in the coarser fractions. The clay mineral and limonite fraction shows two points of concentration; in the coarsest fraction (0.02 to 0.01 mm.) and the finest fraction (—0.0005 mm.).

In sample 2 there is a pronounced concentration of the total clay substance in the 0.02 to 0.005 mm. grade size. Only about 10 per cent of the total clay substance occurs in particles smaller than 0.002 mm. which is frequently considered the upper size limit of true clay. Quartz is almost as abundant as the clay minerals plus limonite, and all constituents show a great concentration in the sizes coarser than 0.005 mm.

The clay substance of sample 3, like sample 2, is chiefly composed of particles coarser than 0.005 mm. Only about 15 per cent of the clay substance is found in particles finer than 0.002 mm. Quartz is considerably less abundant than the clay minerals plus limonite, and all constituents are concentrated in the sizes coarser than 0.005 mm.

The clay substance of sample 4 is composed chiefly of particles coarser than about 0.002 mm. There is a minor concentration in the —0.0005 mm. grade size. Most of the clay substance is composed of clay minerals plus limonite concentrated slightly in the coarsest and finest sizes. A considerable amount of quartz is present, and it is concentrated in the coarsest sizes.

In sample 5, a large part of the clay substance is concentrated in particles larger than 0.005 mm. Clay mineral plus limonite is more abundant than quartz and is evenly distributed except for a slight concentration of the finer sizes. The quartz is concentrated in the coarsest grades.

A large part of the clay substance of sample 6 is found in particles smaller than 0.001 mm. There is a small concentration in the 0.02 to 0.01 mm. grade size, which reflects the concentration of the minor amount of quartz in this size. The sample is distinctive because of the small amount of limonite plus clay mineral in particles coarser than 0.001 mm., and the great concentration of this material in particles finer than this size.

The clay substance of sample 7 shows pronounced concentrations in the 0.02 to 0.005 mm. and the finest grades. Quartz is slightly less abundant than clay mineral plus limonite, and it is highly concentrated in particles coarser than 0.005 mm. There is little clay mineral plus limonite in the coarser sizes, this material being concentrated in the sizes finer than about 0.002 mm.

The clay substance of sample 8 shows a high concentration in the coarsest size with decreasing amounts in successively finer sizes. About half of the clay substance is quartz in particles concentrated in the coarsest grade sizes. The limonite plus clay mineral is evenly distributed throughout the entire clay substance except for a slight concentration in sizes between about 0.005 to 0.0005 mm.

DISCUSSION OF RESULTS

The analytical data show that in all samples very little quartz occurs in particles smaller than 0.002 mm. and that most of it is present in grains coarser than 0.005 mm. Particles of quartz are angular in shape, and they do not add to the bond strength of a sand. If the clay substance were defined with an upper limit of 0.002 mm., quartz grains would be largely eliminated and the clay substance would be more nearly composed of clay minerals and limonite, which are the materials determining bonding strength.

The clay mineral plus limonite component of the clay substance usually is found in particles smaller than 0.002 mm. However, in some samples much of the clay mineral and limonite is present in particles larger than 0.002 mm. These larger particles are aggregates of smaller clay mineral flakes bound rather loosely together by limonite. In general these materials add little to the strength of a sand when they are present in aggregates. When a sand is mulled or revivified there is a tendency to break up the aggregates thereby releasing the component particles which then add to the strength of the sand. Thus, a sand containing aggregates may maintain its strength or even increase it for the first several heats. As the sand is used, aggregates are broken up and bond is developed which may more than compensate for the bond burned out during the first several heats.

It has long been known that all sands with the same amount of clay substance do not have the same strength. The absence of a close correlation between amount of clay substance and green compression strength is shown by the data in table 1. Thus samples 1 and 3 have about the same amount of clay substance whereas the green compression strength of sample 1 is 18 lb. per sq. in. as compared with 13.5 lb. per sq. in. for sample 3. Sample 6 has only one third as much clay substance as sample 3, but has a green compression strength about equal to that of sample 3.

The variations in size-grade distribution and in relative amounts of quartz and clay minerals plus limonite within the clay substance explain to a considerable extent the absence of a close correlation between physical properties and amount of clay substance. For example, the clay substance of sample 1 contains only a small amount of a constituent (quartz) which does not add to its bonding power. Also in sample 1 a large amount of the clay mineral plus limonite is in the finest size grade (−0.0005 mm.) and it is well recognized that the finer the size of the particles of a given type of clay mineral the greater its bonding power. In comparison the clay substance of sample 3 contains a large proportion of quartz and a comparitively small amount of the clay mineral plus limonite in a fine size. It follows, therefore, that the bonding power of the clay substance of sample 3 would be less than that of sample 1. This correlation between the strength of the sand and the constitution of the clay substance is further substantiated by the fineness test results in table 2. The fineness test shows that sand No. 1 is coarser grained than sand No. 3. Because of the composition of its clay substance, the coarser sand (Sample 1) has the higher green compression strength.

TABLE 2.—Clay Substance and Fineness Tests of the Molding Sands

Sieve Size	Per cent							
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
40..........	0.8	0.8	0.4	2.0	0.0	0.4	2.8	0.2
70..........	3.4	2.8	0.6	22.2	0.8	7.8	20.2	0.4
100..........	51.0	8.4	21.6	37.0	21.6	55.8	41.0	2.4
140..........	12.0	4.0	34.6	3.6	9.2	12.6	2.4	1.2
200..........	6.0	19.4	19.4	2.6	12.0	8.0	1.6	2.6
270..........	1.6	27.0	1.0	1.2	13.0	3.0	0.8	4.0
−270..........	5.2	26.8	3.2	10.2	26.6	5.8	5.2	42.2
Clay..........	20.0	10.8	19.2	21.2	16.8	6.6	26.0	46.6
Total..........	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.6
A.F.A. Fineness No....	96	194	125	95	158	95	79	266

Sample 6 shows a very large proportion of its clay substance in the finest grade size and comparatively little quartz whereas the clay substance of sample 3 has a large amount of quartz and a small amount of material in the −0.0005 mm. grade size. This explains why sample 6 has a green compression strength about equal to that of sample 3 which has several times as much total clay substance. Again, the correlation is supported by the fineness test results in table 2 which show that sample 3 is a finer grained sand than sample 6. On the basis of fineness tests alone, sample 3 should have a much higher green compression strength than sample 6. The fact that it does not have much higher strength emphasizes the important effect of the composition of the clay substance on bonding properties.

Sample 2 has a small amount of clay substance, and the clay substance has a large amount of quartz and a small amount of clay mineral and limonite in the finest sizes. The low green compression strength of this sand is, therefore, explained. The importance of the composition of the clay substance is again emphasized by the fineness tests of sample 2 (table 2). Sand No. 2 is a fine-grained molding sand and on this basis alone a greater green compression strength would be expected. The size of the clay particles and the large amount of quartz in the clay substance, however, cause the strength to be low. A further check of tables 1 and 2 and figures 1 to 8 shows that all the molding sands investigated exhibit the same general correlation between their green compression strength and composition of clay substance as the ones selected and quoted herein.

TABLE 3.—Composition of the Clay Mineral Plus Limonite Portion of the Clay Substance

Sample	Composition
1.	Kaolinite VA; illite A; limonite A.
2.	Kaolinite A; illite A; limonite A.
3.	Kaolinite VA; illite (?); limonite A.
4.	Kaolinite VA; illite A; limonite VA.
5.	Kaolinite A; illite A; limonite VA.
6.	Illite VA; kaolinite (?); montmorillonite (?); limonite C.
7.	Kaolinite A; illite A; montmorillonite (?); limonite A.
8.	Illite VA; kaolinite A; limonite C.

VA=40 per cent +;   A=40-20 per cent;
C=20 per cent −.

Variations in the relative abundance of quartz and clay minerals plus limonite and in the size-grade distribution within the clay substance are not the only factors tending to prevent a close correlation between amount of clay substance and physical properties. Another factor is the variation in the type of clay mineral present. In a previous paper,[6] it has been shown that the bonding power of a clay will vary depending on whether illite, kaolinite, or montmorillonite is the constituent of the clay. The identity of the clay minerals, their relative abundance, and the relative abundance of the limonite are given in table 3. It is evident from this table that the clay mineral in all the samples is essentially a mixture of kaolinite and illite. Samples 6 and 7 also appear to contain montmorillonite. The relative amounts of these clay minerals and the character of the illite would have to be determined in considerable detail before a close correlation with physical properties could be made.

SUMMARY

It has been shown that there is considerable variation in the size-grade distribution within the clay substance of molding sands, in the relative amounts of quartz, clay minerals, and limonite which compose the clay substance of different sands, and in the size-grade distribution of these mineral constituents in the clay substance of various sands. These variations explain to a considerable degree the absence of a close correlation between amount of clay substance and physical properties of natural molding sands.

The quartz grains are concentrated in the coarser fractions of the clay substance, and only a very small amount of quartz is found in particles smaller than 0.002 mm. The clay minerals and limonite occur in all sizes within the clay grade, and are frequently concentrated in the coarsest (0.02 to 0.01 mm.) and finest (−0.0005 mm.) fractions. These materials in the coarsest fraction are present as aggregates which are broken down on using so that strength is developed in the sand during the first few times the sand is used.

[6]Grim. R. E., Elements of the petrographic study of bonding clays and of the clay substance of molding sands: Trans. Am. Foundrymen's Assoc., vol. 47, No. 4, pp. 895-908, 1940; see this Rept. Inv., pp. 5-11.

The clay minerals in the sands investigated are kaolinite and illite. Two of the sands also appear to contain small amounts of montmorillonite.

ACKNOWLEDGMENTS

DISCUSSION

Presiding: H. S. WASHBURN, Plainville Casting Co., Plainville, Conn.

H. L. DAASCH[1] (*Written discussion*): The contentions of the authors might be stated: (1) quartz particles should not be considered effective in bond strengths and (2) equally coarse aggregates of true clay minerals are ineffective in bond strength. These lead to (3) sub-micron clay minerals plus limonite are "chiefly responsible for strength properties of the sand." A number of comparisons will be made on these premises.

Samples 1 and 3 are noted in paragraph 25 of the paper. Table 3 shows quite similar clay mineral composition. If less than one micron size clay mineral content is considered for each, we find a ratio of approximately 4:1; a ratio much different than the strength ratio of 18:13.5.

Samples 6 and 3 are also compared in paragraphs 25 and 27 (pp. 19, 20). Note however, that if clay which is smaller than one micron is considered, a ratio of such clay contents is practically 2:1. Yet strength ratio is 12.5:13.5.

Again, compare samples 2 and 5. The below one micron size clay content is approximately in the ratio of 1:5 while the strength ratio is 7.5:11.0. Table 3 shows very similar clay composition.

The writer does not feel that conclusions should be too quickly drawn on the data now available on clay. For example, kaolinite should, according to Grim[2], occur in particle sizes larger than 1 micron. Grim indicates further that illite is most likely to occur in similarly 1 micron and larger particles. Let us now consider samples 1, 2, 3 and 5 which have been compared in previous paragraphs. If kaolinite is eliminated and illite similarly but reasonably not considered because of the likelihood of greater than 1 micron size; we have left primarily limonite in sub-micron size. In three of the four cases the percentage of this limonite is 20-40 per cent. According to the premises of the authors, we would conclude that such limonite would have to account for strength property characteristics.

Again, let us consider statements of Casberg and Schubert[3] and Grim[2] which indicate that base exchange capacity is a criteria of strength properties. Consider further the statements of Grim[2] that kaolinite has relatively low ionic exchange and that illite may often be similarly low. This would bring us to the peculiar conclusion that base exchange variations for the samples 1, 2, 3 and 5 would be accounted for by (1) low exchange capacity material or (2) by limonite.

The writer does not, of course, concur in these conclusions. They are based on generalized statements propounded by the authors in the present paper and in the references quoted.

The point the writer would make is that a "general correlation between green compression strength and composition of clay substance" is not necessarily shown by the data submitted. When viewed in the light of preceding paragraphs we do not "explain to a considerable degree the absence of a close correlation between amount of clay substance and physical properties."

The writer has produced a wide variety of molding sand strength properties by adjustment or change in sand component without any change in type or amount of bond material. Variations in molding sand strength properties need not involve ipso facto any differences in the clay.

Finally, the writer would like to ask the authors if any control is offered in the use of the pipette size analysis and the A.F.A. strength tests which would permit a correlation study as made in the paper. This query is prompted by a recent report by Grim[4]. After discussing the effect of water in fineness and use tests, Doctor Grim writes: "In such correlation work, the objective should to determine the effective particle size i.e., the particle size of the clay as it is usually used." So far as the writer can determine, the authors have neglected this previous admonition in the present correlation study.

A. SAMUEL BERLIN[5] (*Written discussion*): This paper, like others by the same authors, is extremely interesting. It constitutes a valuable contribution on the influence of clay particle size on green strength of molding sands. Since the increase in the green strength depends, to a certain extent, upon the breaking down of the large size particles into smaller ones as for example, the mineral kaolinite, I think it would be advantageous to find a rapid method to determine the chemical and mineral content of the clays so that we would be able to control the green strength of the molding sands in those cases where these factors are important.

Having an economical and positive method of controlling the particle size of the clay so that it would approach the (—0.0005 mm.) fraction, I think would be the solution of quite a few of our molding difficulties that are attributed to green strength failure.

[1]Associate Professor, Dept. of Mechanical Engineering, Iowa State College, Ames, Iowa.

[2]R. E. Grim, Elements of the petrographic study of bonding clays and of the clay substance foundry sands: Trans. Am. Foundrymen's Assoc. vol. 47, 1940; see this Rept. Inv., pp. 5-11.
[3]Casberg, C. H., and Schubert, C. E., An investigation of the durability of molding sands: Illinois Eng. Exp. Sta., Bul., 281, April, 1936.
[4]Grim, R. E., Relation of the composition to the properties of clays: Jour. Am. Cer. Soc. 22, pp. 141-151, 1939.
[5]American Manganese Steel Division, New Castle, Del.

R. E. Grim and C. E. Schubert (*Reply to written discussions*): Mr. Daasch has arrived at conclusions from our data that are obviously in error because he has failed to understand our statements or has read into them meanings which they do not contain.

We state that "particles of quartz . . . do not add to the bond strength of a sand." The point is made that the bonding power of the clay substance rests in the clay mineral and limonite component and not in the quartz component. We realize, and in fact point out, that the total bond strength of a natural bonded sand is partly dependent on the size of quartz grains which the clay mineral and limonite must bond. This, in no way, argues against the idea that the seat of the bonding power is in the clay mineral and limonite and not in the quartz.

Daasch has somehow read into our statements the idea that only the portion of the clay mineral and limonite occurring in particles less than 0.001 mm. in diameter has bond strength. He then proceeds to show that the ratio of the —0.001 mm. clay mineral and limonite fractions of various sands is not the same as the ratio of the bond strength of the same sands. We state clearly (in par. 23 for example, p. 19) that bond strength rests in the clay mineral and limonite component. Nothing is said anywhere that only —0.001 mm. clay mineral and limonite has bond strength. What is stated is that the bonding power of this component of the clay substance tends to increase as the particle size decreases. The ratio between the —0.001 mm. clay mineral and limonite for different sands should, of course, not be the same as the ratio of the bond strength of the same sands because this —0.001 mm. material does not alone determine strength of the sands even when the clay minerals are the same. As pointed out all the clay mineral plus limonite component has strength, the fineness of the quartz must be considered, and the character of the exchangeable base also exerts an influence. What we believe our data show convincingly is that the relative total amount of clay mineral and limonite in the clay substance of a molding sand is important in determining its strength, and also that the initial strength of two molding sands, equivalent in every way except in the size distribution of the clay mineral and limonite particles and aggregates will be different—the one containing these components in the finer size having the higher strength.

Grim states that kaolinite occurs in particles rarely smaller than —0.001 mm. and that most illite occurs in particles about this same size. Grim also states that some illite occurs in finer particles. Daach concludes, as the clay minerals in the samples are chiefly kaolinite and illite, that there are no clay minerals in the —0.001 mm. size grades and that it is all limonite. As Daasch has thought only—0.001 mm. material has bonding power, he concludes that the bonding power is only possessed by the limonite. This is, of course, an erroneous conclusion.

Some of the kaolinite and illite occur in the —0.001 mm. fractions and the entire clay mineral plus limonite fraction is responsible for bonding power. Grim is perhaps responsible for Daasch's false conclusion here, by not stating that kaolinite rarely occurs in particles smaller than *about* 0.001 mm. The point that Grim wished to emphasize was that kaolinite and most illite tend to occur in particles larger than *about* 0.001 mm., and that they are not easily broken down by agitation in water into particles much smaller than this size. This is

a generality encountered by all students of clay mineralogy.

Kaolinite is shown to have a low base-exchange capacity, and illite is known to have low or moderate base-exchange capacity. These are the clay mineral components of the samples studied. We have not determined the base-exchange characteristics of our samples, and consequently do not know whether such determination would substantiate or deny the findings of Casberg and Schubert. Because the clay minerals are those having low capacity seems to us to be no reason to conclude, as Daasch has done, before any determinations are made that such determinations would not agree with Casberg and Schubert.

In reply to Daasch's question about particle size analysis, we would say that we followed the Bureau of Standards procedure to which reference is made. We point out that the pipette analyses show some clay mineral and limonite in all size grades and that it is frequently concentrated in the coarse (because of aggregates) and in the finest size grades. These fractionations were made to show first the particle size distributions of quartz in the clay substance. It should be emphasized that Grim's statements of "effective particle size" referred to clay minerals only and not to quartz. The fractionations were made also to determine the particle size of the clay minerals and limonite when prepared by a method suggested for molding sands. The authors made no attempts to correlate the size grade determinations *in detail* with the bonding properties. This cannot be done in detail because of the "effective particle size" concept, and, as pointed out before, because other factors control bond strength. The justifications for the statement of Daasch that some general conclusions cannot be recognized because details cannot be worked out is not clear to us. In our minds the discussion of the break down of the aggregates with the liberation of bonding power as the sand is used is an illustration of the importance of "effective particle size" rather than a neglect of it.

Finally we feel that the data presented by us show that the abundance and size grade distribution of the quartz and clay mineral plus limonite "explain *to a considerable degree* the absence of a close correlation between amount of clay substance and physical properties of natural molding." We inserted the expression "to a considerable degree" because these "are not the only factors tending to prevent a close correlation" (paragraph 29, p. 20).

In reply to Mr. Berlin we wish to say that at the present time the method for determining the mineral composition of the clay substance of molding sands and for studying the size grade distribution of the clay mineral particles is long and somewhat involved. The method embodies a combination of size-grade fractionation and petrographic analysis. The petrographic analysis identifies the minerals by X-ray and optical analytical data. Mr. Berlin is quite correct, it would be very advantageous to find a shorter method for this work, and we hope that this may be possible.

Member: Is it possible to separate the limonite from the clay minerals?

Dr. Grim: There are ways of getting rid of the iron oxide. You can remove it, but it is frequently impossible to remove it quantitatively and still retain the clay minerals with their original character.

H. Ries[6]: In paragraph 6, the authors state that the size-grade distribution of the grains was de-

termined with a pipette. Have the authors in their laboratories ever used the hydrometer method?

Dr. Grim: Yes, we have used the hydrometer method. The chief reason for the pipette method here was to obtain fractions for microscopic study. In the case of the pipette, you draw off a certain amount that represents the material finer than a given size grade and then you have something to study for the identification of the constituents. We have no objection to the hydrometer method. We chose to use the pipette method simply because it gave us samples for mineralogical analysis.

Member: Would the amount of limonite present be indicative of the effective life of the clay?

Mr. Schubert: According to the hydration and dehydration curve, I might answer it in this way. Limonite breaks up at a very low temperature and gives up its water of crystallization or what might be called water crystallization. Therefore, a lot of limonite in any natural sand or any bonding substance should cut down the life of the sand. Now, we have not yet determined the durability or life

of sands of the natural variety. We reported[7] at the 1937 convention on what we call synthetic sands. Those were of the montmorillonite and kaolinite type and we did not include plain limonite and silicia sand. From the hydration curves alone, we know that limonite, being a hydrated ferric oxide, does give off its water at very low temperatures and in ordinary casting work, you would expect that sand, if it had an appreciable amount of it in there, to burn out very readily, and therefore its life would be cut down to some extent.

Member: In these two comparative cases, 1 and 3, could the author give us an indication as to the difference in the amount of limonite?

Mr. Schubert: That is contained in Table 3. The limonite was about 20 per cent in both samples.

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[6]Cornell University, Ithaca, N. Y.

[7]Schubert, C. E., A correlation of the physical and chemical properties of clays with the durability of molding sands: Trans. Am. Foundrymen's Assoc. vol. 45, pp. 661-688, 1937.

THE RELATIONSHIP BETWEEN THE PHYSICAL AND MINERALOGICAL CHARACTERISTICS OF BONDING CLAYS†

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ABSTRACT

Data are presented to show that the kind and amount of clay mineral in a clay are the most important factors determining its bonding strength. The relation between these factors is discussed. The problem of the break up of the clay mineral in clays, such as might be brought about by mulling, is analyzed in relation to bonding strength.

INTRODUCTION

The object of the investigation reported herein was to study the fundamental factors controlling the variations in the bonding properties of clays. It is a well recognized fact that not all clays possess the same bonding characteristics, but the factors that determine the variations have not been well understood. This report is the fourth[1, 5, 6]* of a series reporting the results of the Illinois State Geological Survey's project for the investigation of the fundamental properties of bonding clays and molding sands.

In recent years, it has been shown that most clays and shales are made up of extremely small particles, frequently less than 0.001 mm. (1/25000 in.), of a limited number of minerals known as the clay minerals. Stated another way, clays and shales are essentially aggregates of extremely minute particles of one or more of the clay minerals. The most common clay minerals are noted in table 1.

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*Superior numbers refer to bibliography at end of paper.
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In addition to clay minerals, clays and shales also may contain varying amounts of quartz, organic material, limonite (hydrated ferric iron oxide), etc. Of the non-clay mineral constituents, quartz, in the form of grains, is by far the most abundant and most common. Clays differ from each other fundamentally in the clay minerals that compose them, in the amount of admixed quartz or other non-clay mineral constituents, and in their texture (size of particles, etc.).[1] It is the purpose of this report to present the results of a study of the influence of these fundamental differences between clays on their bonding characteristics.

PROCEDURE

In the past eight years, the complete mineral composition of a large number of clays and shales has been determined by x-ray and microscopic methods in the laboratory of the Illinois State Geological Survey. From these clays and shales, a group was selected for the present investigation that exhibited wide variations in composition and texture. The clays selected are not all commercial bond clays. The clays used were chosen so

Table 1.—Chemical Composition and Occurrence of Common Clay Minerals

Name	Chemical Composition*	Occurrence
Montmorillonite	$(OH)_4$ Al_4 Si_8 O_{20} xH_2O	Bentonites, gumbotils, etc.
Illite	$(OH)_4$ K_y $(Al_4 \cdot Fe_4 \cdot Mg_4 \cdot Mg_6)$ $(Si_{(8-y)}. Al_y)$ O_{20}	Shales, gumbotil, underclays, etc.
Kaolinite	$(OH)_8$ Al_4 Si_4 O_{10}	Underclays, fire clays, china clays, etc.

*Certain substitutions are possible in these general formulae. For details see Grim, R. E., Relation of the composition to the properties of clay: Jour. Am. Ceramic Society, vol. 22, pp. 141-151, 1939; reprinted as Illinois Geological Survey, Circular 45, 1939.

that the results would provide a broad picture of the effect of different characteristics of clays on their bonding properties.

The green compression strength of each sample, at several different moisture contents, was determined using 8 per cent clay and 92 per cent sand (except for the bentonite sample when 4 per cent clay and 96 per cent sand were used). These determinations were carried out according to A. F. A. standard procedure except that the sand* used had a fineness number of 56 instead of 50.

For each sample, the amount of material coarser than the A. F. A. clay grade[2] and the size grade distribution within the A. F. A. clay grade were determined by the pipette method (modified after Jackson and Saeger[3]). Any method for the determination of the size grade distribution of a clay or shale requires that the clay or shale be first broken down in water into a suspension. The results obtained are always dependent to some degree on the amount the clay or shale has been disaggregated in water prior to the analysis. In other words, widely different size grade distribution determinations may be obtained from a single clay by the use of different amounts and kinds of disaggregation.

In the present research, great care was used to carry out the disaggregation of all samples in exactly the same manner so that the results would be comparable. The disaggregation procedure followed was mild, *i. e.,* no attempt was made to break the clays or shales down to anything like their ultimate particle size. The mild procedure was followed because in the actual use of clays or shales for rebonding, they are in general not immediately broken down to their ultimate particle size. It was felt that the following procedure disaggregated the clay to about the same degree as in the actual use of the clay for rebonding and, therefore, that the results would be particularly significant in an understanding of the variations of the bonding properties of clays or shales.

The clay or shale was first ground to pass a 70-mesh screen and then soaked in water for 7 days. During the soaking period, the clay and water were agitated about once every 12 hours. Ammonium hydroxide (NH_4OH) was used as the dispersing agent.

*The sand used comes from the Ottawa, Ill., district and is regularly sold as "bond" sand.

ANALYTICAL DATA

The determinations of maximum green compression strength, moisture content at maximum strength, quantity of clay minerals, clay mineral composition, and quantity of material in the A. F. A. clay grade are given in table 2. The per cent of clay mineral in the entire sample was determined by means of microscopic examination. In some clays and shales, the clay minerals occur in individual particles and aggregate masses that are larger than the upper size limit of the A. F. A. clay grade, *i.e.,* 0.020 mm.

The quantity of A. F. A. clay given in table 2 is that portion of the sample shown by the pipette analyses to be less than 0.020 mm. in diameter. The disaggregation procedure preliminary to the pipette analyses was a very mild one which did not reduce all the clay mineral aggregates or large individual particles in all samples to a size smaller than 0.020 mm. As a consequence, the table shows the total amount of clay mineral to be more than the A. F. A. clay for some samples.

The determinations of the size grade distribution of each sample within the A. F. A. clay grade are given in figure 1. The distribution curves in figure 1 were constructed by the graphic differentiation method[4] from cumulative curves plotted from the results of the pipette analyses. The distribution curves show the amount of material between any given size limits by the proportion of the area under the curve between the given size limits to the area beneath the entire curve.

For example in curve No. 2, the area *(EFSC)* beneath the curve and between vertical lines constructed at the 0.020 mm. and 0.010 mm. points is 11.2 per cent of the area beneath curve *(EJNC)*, plus the rectangular areas *(ABCD* and *KLMN)* and therefore 11.2 per cent of the sample is in the 0.020 mm. to 0.010 mm. grade size. The area of the rectangle *(KLMN)*, on the right, in proportion to the area under the curve *(EJNC)* plus the area of the rectangles *(ABCD* and *KLMN)* represents that portion of the sample smaller than 0.005 mm. in size (12.7 per cent for sample No. 2). The rectangle *(ABCD)*, on the left for sample No. 2, has an area equal to 33.9 per cent of the area under the curve *(EJNC)* plus the areas of rectangles

TABLE 2.—Properties and Clay Mineral Constituents of Clay Found in Various Locations

Sample No.	Location	Per Cent Clay in Strength Test Mixture	Maximum Green Compression Strength lb. per sq. in.	Per Cent Water at Maximum Strength	Per Cent A.F.A. Clay Grade††	Per Cent Clay Mineral in Total Sample	Clay Mineral Constituents
1	Bentonite, Wyoming............	4	9.6	1.00	95.0	95	Montmorillonite—100
2	Eocene clay, Pulaski Co., Ill..	8	18.0	3.12	66.1	70	Montmorillonite—90*
3	Pennsylvanian underclay Grundy Co., Ill.	8	13.6	1.92	81.9	90	Illite—80†, Kaolinite—20
4	Pennsylvanian underclay Madison Co., Ill.	8	12.0	1.70	56.0	90	Kaolinite—85, Illite—10, Montmorillonite—5
5	Pennsylvanian underclay Madison Co., Ill.	8	9.9	1.43	65.6	75	Kaolinite—85, Illite—10, Montmorillonite—5
6	Pennsylvanian shale Green Co., Ill.	8	8.6	1.68	49.0	90	Illite—90, Kaolinite—5, Montmorillonite—5
7	Pennsylvanian underclay Grundy Co., Ill.	8	8.2	1.41	64.8	75	Kaolinite—65, Illite—35
8	Pennsylvanian underclay, Ohio	8	8.2	1.5–2.2	88.7	75	Kaolinite—75, Illite—25
9	Residue, Ordovician dolomite Kane Co., Ill.	8	8.2	1.68	75.5	70	Illite—100
10	Pennsylvanian shale St. Clair Co., Ill.	8	7.2	1.67	72.1	90	Illite—80, Kaolinite—20
11	Pennsylvanian shale Tazewell Co., Ill.	8	6.3	1.55	91.8	80	Illite—90, Kaolinite—10
12	Pennsylvanian shale Sangamon Co., Ill.	8	6.1	1.60	65.5	70	Illite—90, Kaolinite—10
13	Pleistocene clay Livingston Co., Ill.	8	3.4	1.60	69.4	50	Illite—100
14	Pleistocene clay Livingston Co., Ill.	8	2.4	1.20	43.0	30	Illite—100

*This sample contains a small amount of another clay mineral that cannot be identified positively. It appears to be either chlorite or kaolinite.
†The illite in this sample is unusual because of its low content of potassium oxide and certain of its physical properties. See Journal American Ceramic Society 22, pp. 157-164. 1939.
††This is the amount of material finer than 0.020 mm. obtained by the pipette analytical procedure used in the present study.
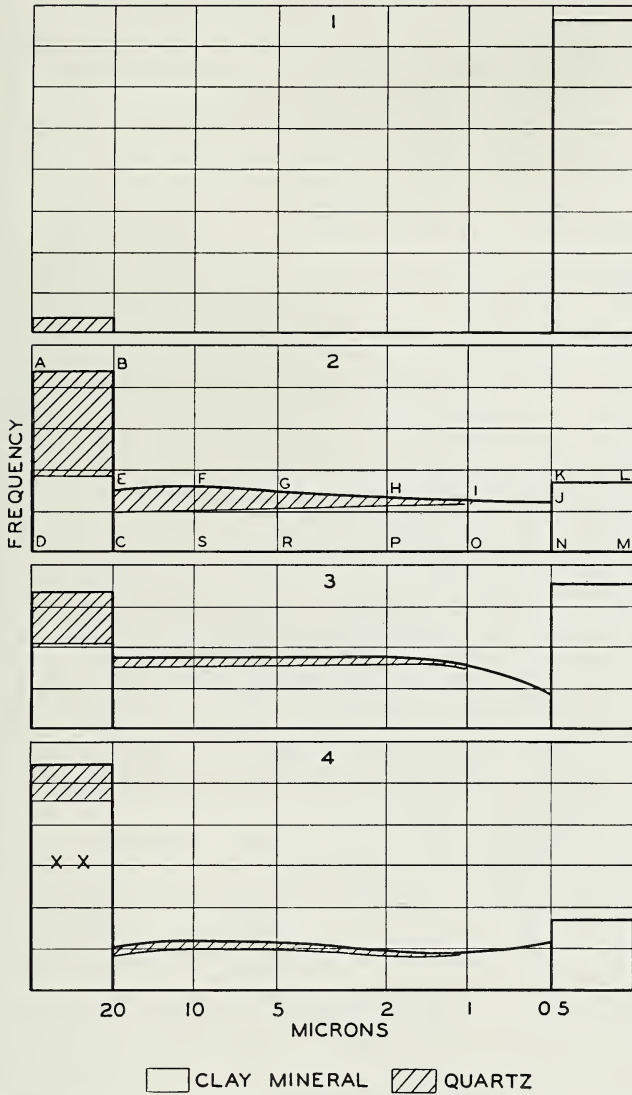
Fig. 1—Size Grade Distribution Curves. 1 Micron is Equal to 0.001 mm. For the Significance of the "XX" See Text Below.

(ABCD and KLMN) and, therefore, indicates that 33.9 per cent of the sample is composed of particles larger than 0.020 mm. in size.

In the curves in figure 1, the cross-hatched areas represent the amount of calcite, the diagonal ruled areas represent the amount of quartz, and the remaining area represents the amount of clay mineral. The amount of these minerals in the samples as a whole or in the individual size grades can be obtained from the curves by comparing areas. The clay mineral material occurring in the coarser size grades, for example +0.005 mm., may be either aggregates of smaller particles or individual particles of the size indicated. Where the size grade is composed primarily of individual particles of clay minerals rather than aggregates, the designation "XX" is used.
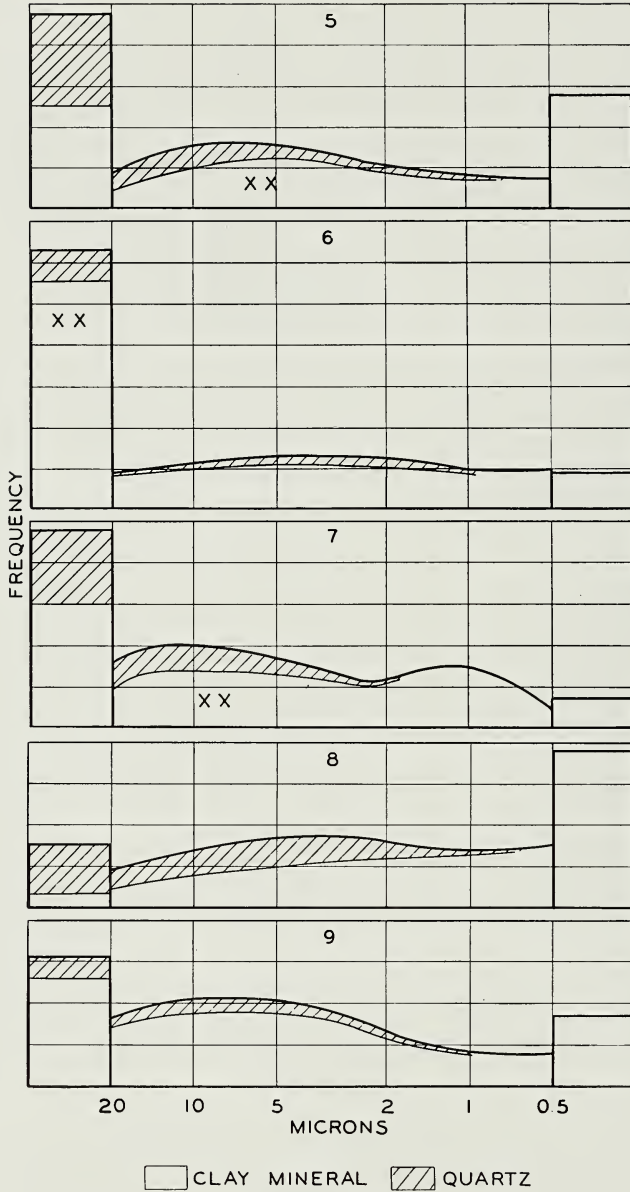
Fig. 1 Continued.

SIGNIFICANCE OF DISTRIBUTION CURVES

The size grade distribution curves in figure 1 show that there may be a tremendous variation in the size distribution of particles for different clays. Thus, one clay material (No. 1) has most of its particles smaller than 0.005 mm. whereas another (No. 12) has very few particles finer than this size. Some samples (Nos. 1 and 11) have very few particles coarser than the A. F. A. clay grade, *i.e.,* 0.020 mm., whereas other samples (Nos. 4 and 6) have many particles coarser than this size. One clay (No. 2) has a very even distribution of particles between 0.020 mm. and 0.0005 mm., whereas another one (No. 11) has an uneven distribution of particles between these sizes.
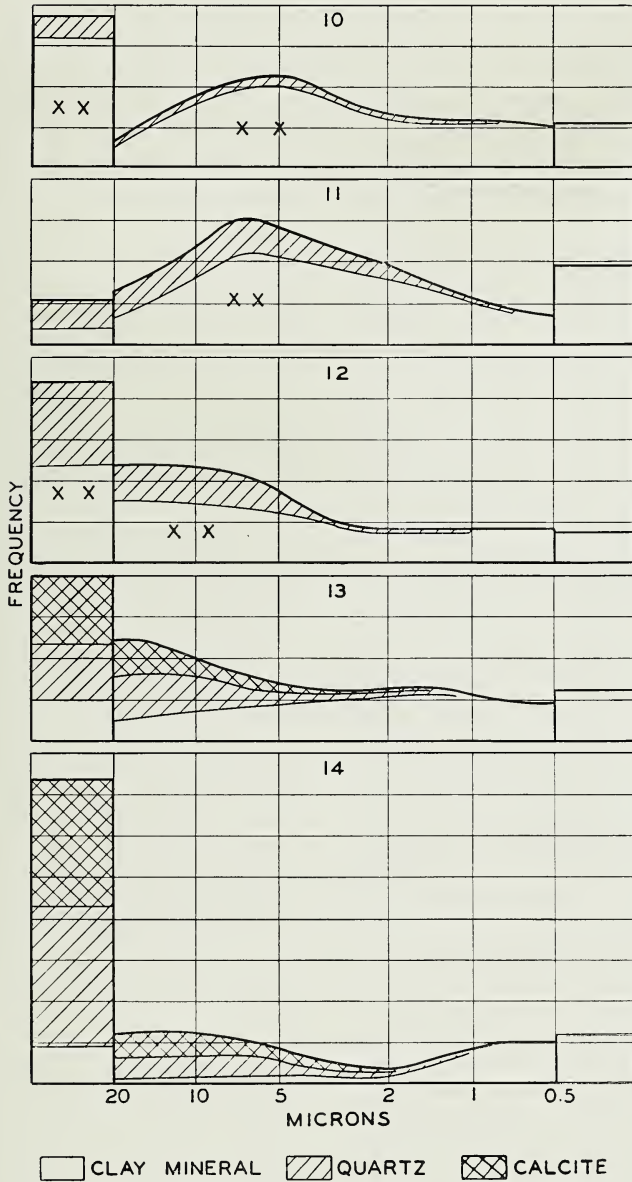
FIG. 1 Continued.

The distribution curves in figure 1 are arranged in the order of decreasing green compression strength of the clay materials they represent, No. 1 having the greatest and No. 14 the least strength. A critical analysis of the size distribution data of these samples in relation to their bonding strength, brings out the fact that there is no precise correlation between any single size distribution characteristic, or combination of them, and the bonding strength of the clay materials. For example, there is no correlation between the amount of A. F. A. clay grade as determined in this study and the green compression strength; also there is no correlation between the amount of material finer than 0.0005 mm., and the green compression strength. This means that some other factors are dominant in controlling the bonding strength of clay materials. It will be shown presently that the amount

and character of the clay mineral content are the dominant factors.

One might conclude, on the basis of theoretical considerations and microscopic study of clay-bonded sands, that a clay composed chiefly of extremely minute particles (less than 0.001 mm.), or of larger particles that broke down immediately to such minute particles when used, would have the highest bonding power, other factors being equal. This conclusion would seem to follow, because smaller particles would give a greater total surface area in the clay for bonding purposes, and microscopic study shows that a very fine-grained clay evenly coats the sand grains while another clay of larger particle size coats the quartz grains irregularly with many large clay lumps between grains that can have little influence on the strength of the sand-clay mixture.

In the clays studied, the sample composed of the finest particles has the greatest strength (No. 1). However, sample No. 2 with about the same clay mineral composition is composed of much larger particles and yet has about the same strength as sample No. 1. Data from other samples support the conclusion that a raw clay need not necessarily be composed of extremely minute particles (−0.001 mm.) to be a good commercial bonding clay. In fact a clay composed of somewhat coarser particles of clay mineral may have certain advantages over one composed only of extremely minute particles. If the coarser clay contains clay mineral particles that break down into minute particles with fair rapidity when the clay is worked, the clay will probably have better durability because breaking down of the clay mineral particles will continue to provide new bonding surfaces as the clay is being used.

It should be emphasized that only the clay mineral particles in a clay possess bonding strength[5], and that only the clay mineral particles can easily and readily be broken into smaller sizes when the clay is worked, e.g., in mulling. The clay mineral particles are flake-shaped and their breakdown tends to take place by cleavage of the flakes. Although clay mineral particles tend to occur in clays generally in particles less than 0.002 mm., individuals and aggregates are frequently 0.020 mm. or more in diameter in many clays and shales.

In general the clays studied that have a relatively even distribution of particles, between 0.020 mm. and 0.0005 mm., also have high green compression strength. The explanation seems to be that such clays do not contain large amounts of non-clay mineral material in particles smaller than 0.020 mm. and also that they are composed of clay mineral particles and aggregates that break down with reasonable rapidity into extremely minute particles. A critical consideration of the data indicates that a clay composed of large clay mineral particles that does not break down into very fine particles is not a satisfactory bonding clay. On the other hand a satisfactory bonding clay is not necessarily one composed only of very fine particles, or of larger particles that break down immediately when the clay is first used. A clay composed of particles that break down with intermediate ease is apt to be a most satisfactory bonding clay (other factors of clay mineral composition, etc., being equal).

Those clays studied that show an irregular distribution between 0.020 mm. and 0.005 mm. are also those that contain a large amount of non-clay mineral material, or an abundance of large clay mineral particles that do not break down easily. In either case the sample has low bonding value because it contains a large proportion of material with little or no bonding power.

SIGNIFICANCE OF CLAY MINERAL COMPOSITION

Data obtained in the present work substantiate the conclusion of an earlier paper[5] that the clay mineral composition is the most important factor in determining the bonding strength of a clay. The data also verify the conclusion that montmorillonite is the clay mineral providing the highest strength (samples 1 and 2), and that the presence of a small amount of montmorillonite in a clay will raise the bonding strength out of all proportion to the actual amount of the montmorillonite. This is illustrated by comparing the green compression strength of samples 4 and 5, which contain small amounts of montmorillonite in addition to kaolinite and illite, with samples 7 to 12 which contain only kaolinite and illite.

The present data show that kaolinite and most illite materials have much lower bonding strength than clays composed of montmorillonite, and that kaolinite clays have

higher strength than most illite materials. The characteristics of illite vary within wide limits and the data indicates that occasionally an illite clay may have very high bonding power. For example, sample No. 3 composed largely of illite has very high strength. Chemical data, obtained in another study, show that there is a range in the potassium oxide (K_2O) content of the illite clay minerals, and that in general clay materials composed of illite with relatively high K_2O content have low green compression strength.

It is significant that one of the attributes of montmorillonite and the certain illite (*e.g.,* sample No. 3) is that they either occur in extremely minute particles or in larger particles that break down easily into very small particles. Kaolinite and illite, particularly illite with a high K_2O content, tend to occur in particles of larger size that break down with difficulty into particles of very small size. One, but probably not the only reason for the difference in bonding power of the different clay minerals, is the variation in the ease with which they break down into very fine particle size.

A comparison of samples 2 and 8 emphasizes the importance of the clay mineral composition in determining bonding strength. Sample No. 2 has much less material finer than 0.0005 mm. and much more material coarser than 0.020 mm. than has sample No. 8, yet sample 2 is the stronger clay because it is composed of montmorillonite. In both samples the actual amount of clay mineral is about the same.

INFLUENCE OF THE AMOUNT OF CLAY MINERAL

The data in table 2 illustrate that there is a relation between the amount of clay mineral in clay materials of the same clay mineral composition and their bonding strength. Thus samples 13 and 14 with low clay mineral content have very low bond strength. The data suggest further that the non-clay mineral content does not reduce the bond strength of a clay or shale very much unless there is more than about 30 per cent of it present. In other words non-clay mineral matter tends to have little effect on bond strength unless it makes up more than 30 per cent of the total clay material.

SUMMARY

The green compression strength of fourteen clays of widely different compositions was determined, at 8 per cent clay and 92 per cent sand (except bentonite—4 per cent clay and 96 per cent sand).

Pipette analyses of these clays were made using mild disaggregation procedure. These analyses show approximately the effective particle sizes of the clays as they exist when the clay is used in the foundry.

An analysis of the size distribution of the clays in conjunction with their green compression strength shows that those clays which break down with intermediate ease are apt to be most satisfactory (other factors of clay mineral composition, etc., being equal).

A comparison of the kind of clay mineral with bonding strength indicates that clays composed of montmorillonite have the greatest green compression strength. Clays composed of kaolinite and illite have lower bonding strength. An example of an unusual illite clay is given that has high green compression strength. A small amount of montmorillonite present in a mixture with either kaolinite or illite yields a bonding strength out of all proportion to the amount of montmorillonite present

The presence, in amounts greater than about 30 per cent, of such materials as quartz, calcite and/or large clay mineral flakes which do not break down easily causes low bonding strength.

There is a relation between the amount of clay mineral and the bonding strength in clays of the same clay mineral content.

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