PARTICLE SIZE DISTRIBUTION IN CLAYS

By A. L. Johnson *

The identification of the structure of a clay mineral is best accomplished by X-ray analysis. Under certain conditions, however, the differential thermal method (Grim and Rowland 1944), may also be used to identify structure. These are basic methods of determining to what clay group a particular sample may belong. However, the mere fact that a clay mineral has been identified as a member of the montmorillonite group, the kaolinite group, or the illite group, for example, does not solve the problem. Too often, the behavior of one member of a specific mineral family is so divergent from the behavior of another member of the same group, that the question is raised whether or not both may rightly be classified as members of the same family. For instance, two clay samples which indicate by their structure that they are members of the montmorillonite group can differ so widely in their physical characteristics that one may be eminently suitable for use as an oil-well drilling clay, and the other not at all suitable. Because of such irregularities persons interested in clay technology have attempted to further define the clay system.

As the clay-mineral particles are colloidal in size, factors involving the colloidal properties also must be considered in the definition of the system. Therefore, in addition to determining the structure of a clay mineral, it is necessary to examine other physical properties to more closely define the system. The fact that clays are colloidal and exhibit colloidal properties indicates that a variation in these properties could be attributable to variations in the colloidal nature of the substance, and not necessarily to the crystal structure.

It is generally assumed that the factors which affect the colloidal behavior of a clay system are at least fourfold. The first factor deals with the structure; the second, with the surface area; the third has to do with the electro-kinetic or zeta-potential of the system, and the fourth factor deals with the admixed inorganic and organic impurities in the system. Although the effect and influence of the admixed impurities, soluble and insoluble, organic or inorganic, are not fully known, there is little doubt that these impurities can play a major role in altering the properties of a clay. It is not the intent here to consider in detail all four factors which can influence the properties of a clay. Certainly, the subject matter of structure has received adequate attention elsewhere in these proceedings. The consideration of ion-exchange properties and the effect of the type and amount of ions on the electro-kinetic potential still requires knowledge which is not yet available. One reason for the lack of information is the difficulty of determining which of the data on the total ions present in a system apply to exchangeable ions and which do not. When the chemical techniques for making this separation have been resolved, then we can expect a clarification of the role that the ions play in affecting the behavior of members of the clay system.

The particle distribution of a given clay sample and the effect of this distribution on the total surface area are of great importance in determining the amount of colloidal activity to be experienced. The measurement of surface area is also of great importance, as colloidal activity can be related to a definite surface-to-weight ratio. But before surface area can be measured, the dimensions of the particles must be obtained. For this reason, the methods of measuring the size and distribution of the primary particles have been of great interest, and activity in this field has increased in the last decade.

Early in the twentieth century, Zsigmondi developed the ultra microscope and observed not only gold particles in Brownian motion, but also the size of primary particles. As a result of his observations, the use of optical equipment for the measurement of sub-sieve particles received much attention. Direct methods of measurement have been used with great success. Since his work, the direct methods of particle measurement have been superseded, to some extent, by indirect methods which relate the settling of particles through some medium to the diameter of the particle. The relationship between velocity of fall and diameter of spherical particles is given in the following equation:

$$d = k \sqrt{v}$$

where:
  d = diameter
  v = velocity of fall
  k = constant

Although particles of clay are far from spheres, when they are allowed to fall in dilute suspensions without interference, the tumbling motion imparted to the particle by its irregular shape and the viscocity of the medium make it in effect a sphere. For this reason, probably, the data obtained by using the above formula are in good agreement with direct measurements made with optical equipment (Johnson and Lawrence 1942).

Indirect methods of measuring particle distribution fall into at least three classifications: sedimentation, elutriation, or centrifugation. The principal advantage of these methods is that more precise measurements can be obtained than by direct methods using optical equipment.

An important improvement of particle measurement was in the field of direct measurements, where use of the electron microscope, with its high resolving power, superseded some of the indirect methods, especially for determining particle shape. Development of special techniques, such as shadow casting (Williams and Wyckoff 1944, Woodward and Lyons 1951), gave great impetus to the use of the electron microscope for obtaining concrete information regarding the dimensions of clay particles. Up to this time, the calculations of surface area were based on observations involving the oscillations and scintillations of particles observed indirectly. The electron microscope afforded means of direct measurement of the three dimensions of a particle,

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from which the surface area was readily obtained by simple calculations.

In the particle size range down to 25 microns, direct methods involving optical equipment (Dallavalle 1948) are sometimes more adequate than methods involving sedimentation. Between the 25 microns and $\frac{1}{2}$ micron range, sedimentation or elutriation are used to greater advantage than the direct methods involving optical equipment. Below $\frac{1}{2}$ micron, the sedimentation method must be augmented by some means of centrifugation (Norton and Spiel 1938). For extremely fine particles, such as certain montmorillonites, centrifugal methods (Hauser and Lynn 1940; Lyons and Johnson 1947) are almost universally used. Therefore, depending upon the size-range of particles to be observed, one selects the method and techniques based upon the accuracy desired and the time involved in making the measurement.

All indirect methods of particle-size measurement require that the sample be completely dispersed in the medium. This involves not only a careful consideration of the medium and method of dispersion, but a dilution at which particle interference does not take place. This extreme dilution is necessary to insure accuracy in the measurement. In practice, the clay suspension used to determine particle distribution is rarely over 2 percent solids. Such procedures allow a measurement of the size of the primary particles. Data from such measurements, coupled with shape factors, permit the calculation of the surface area of the clay fraction.

The clay systems which are utilized by the soil mechanics, the highway engineers, the agronomists, the ceramists, or others interested in clays, are not those of complete dispersion, however. On the contrary, they are compact mixtures, in many instances containing little or no water. Surface-area calculations which are readily made on completely dispersed systems cannot be made on systems which are compact. The complete definition of the particle size of the system should not take into consideration only the distribution and size of the primary particles, but also the state of aggregation, or the degree of compaction of the primary particles.

The need today is for methods of determining the state of aggregation of the clay minerals. Direct methods of measurement appear to lend themselves to this problem. However, no detailed techniques are available which provide the necessary data. The fact that larger particles of other minerals are usually associated with the clay systems, makes the problem more complex. Undoubtedly, the role of the clay particles with respect to the larger non-clay particles is important, and the state of dispersion of the clay particles greatly influences the system.

Methods of determining the absolute size and distribution of clay samples are available and can be relied upon. From such measurements, calculations of the surface area can be made. However, the restrictions placed on the methods of measurement such as complete dispersion and dilution limit the application of this information. Data on clay systems as they are used in industry would be more useful. Rarely, if ever, are the clay particles in such systems completely dispersed. Therefore, the state of aggregation is of prime interest.

DISCUSSION

J. W. Earley:

In our laboratory we separated a montmorillonite sample into five particle-size fractions ranging in size from 1600 millimicrons to 50 millimicrons. By redispersing each fraction 10 to 15 times and rerunning it through the Sharples super-centrifuge, we were able to increase the minus 50 millimicrons fraction to about 50 percent of the total sample. On the basis of these results would anyone care to comment on the particle size of montmorillonite, illite, or kaolinite?

E. B. Kinter:

Working with the electron microscope, we came to the same conclusion with respect to montmorillonite. If one continues to disperse montmorillonite the particles get finer and finer. It would seem, therefore, that coarse particles are essentially aggregates and that their size reflects the degree of dispersion attained. This does not apply, however, to kaolinite and illite, which do not readily break down into such ultra-fine particles.

W. P. Kelley:

Upon dispersion do individual particles separate from aggregates or are individual lattice layers split off from crystals? In other words do crystals subdivide to the point where they are thinner and thinner, or is it merely a matter of dispersion of aggregates? Possibly the plates become broken crosswise.

G. W. Brindley:

From the shape of the X-ray diffraction bands, particularly the one near 4.5 Å, Méring and I believe that the order of magnitude of the average flake or crystallite is from 200 to 250 Å. I do not think that crystallite dimensions are as large as 500 Å. The *particle* size, of course, may be quite different. I might add here that the shape of a band, generally speaking, depends both on the variation of structure factors with angle and on the size of the flakes. Some bands are more sensitive to structure-factor variation than others. The strong band at about 4.5 Å is dependent mainly on flake size, because in this angular range the structure factor varies rather slowly with angle. If one assumes the flake to be roughly hexagonal in shape, the variation in the intensity of that band can be used to obtain fairly reasonable estimates of the mean flake dimension.

D. M. C. MacEwan:

What would be the effect on the shape of the bands if the layers were bent; is it possible that the spreading of the bands might be due to bending rather than to crystal size? I would like to draw attention to a paper by Mathieu-Sicaud et al. (1951) discussing the electron microscope technique. They suggest that the fundamental particles of montmorillonite are about 300 Å across but that these particles can link together on the edges to form larger particles, mainly with parallel orientation. These large particles, in some cases, showed a tendency towards hexagonal edges. The process of dispersion may cause not only the separation of layers, but the breaking of layers into fundamental particles about 300 Å across.

G. W. Brindley:

Regarding the first question: we have not taken account of any bending of the planes. I do not know what the effect of bending of the lattice would be on the X-ray diffraction. Recent papers by Wilson (1949) and Blackman (1951, 1951a) have considered the question but no application has so far been made to a clay mineral.

With regard to the second question, Méring and I considered that the X-ray diffraction work gave a very satisfactory mean crystal size of the same order of magnitude as the minimum size observed with the electron microscope. The electron microscope indicates that the flakes link together in an edgewise manner but upon dispersion either the edgewise linking is broken or the linking is of such a character that the scattering from adjacent flakes is incoherent. This would indicate that the two linked particles are not crystallographically joined. The flakes are, to a large degree, in parallel orientation but still incoherent from the point of view of X-ray scattering.

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