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STUDIES OF THE CLAY FRACTION IN ENGINEERING SOILS

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SYNOPSIS

PART I-IDENTIFICATION BY DIFFFRENTIAL THERMAL ANALYSIS

This paper is the first in a series of articles concerning the role of the clay fraction in engineering soils, including both the methods of analysis and the application of the results obtained therefrom to the determination and control of the engineering behavior of these soils. The differential thermal method of analysis is presented with the major emphasis on the preparation of samples for analysis so as to increase the sensitivity and accuracy of this analytical procedure.

Sample preparation becomes necessary whenever the clay fraction constitutes only a small percent of the soil or when other constituents are present whose reactions tend to mask those of the clay minerals. The clay concentration may be increased by extracting and analyzing either the soil fraction passing a 270 mesh sieve or the particles less than one micron in diameter. Interfering constituents may be eliminated by the proper treatment, e.g. the removal of organic material from a soil by the use of hydrogen peroxide.

Examples of the thermal patterns obtained by the use of these techniques in some Iowa soils are presented. These patterns are discussed to show what data can be obtained from this relatively simple, rapid method of soil analysis.

PART II—PARTICLE SIZE DISTRIBUTION AND CATION EXCHANGE CAPACITY

This is the second in a series of studies concerning the definition and control of the properties of the clay fraction in engineering soils. This article presents methods for the determination of the particle size distribution down to onetenth micron diameter and below, and for the rapid determination of cation exchange capacity for the whole soil and for the less than one micron fraction. The methods presented have been selected because of their rapidity and simplicity and because they employ equipment which is readily available.

Correlation of the results obtained by these methods cannot at the present be made with soil properties except in a very general manner. However, these methods are accurate and when the basic knowledge relating fundamental clay properties and soil behavior is known they will be valuable analytical tools. Further studies with the purpose of making available the knowledge necessary for the fullest application of analytical rescarch to practical engineering are in progress.

PART I-IDENTIFICATION BY DIFFERENTIAL THERMAL ANALYSIS

It is now well established that the clay fraction of soil is the seat of varied and vigorous reactions which greatly influence the behavior of soil as an engineering material. Experimental evidence indicates that such properties as plasticity, adsorption, shrinkage, swelling, and bonding strength are largely governed by the amount and nature of the clay material.

It is the opinion of the authors that many of the problems encountered in soil engineering can best be attacked through a comprehensive study of the clay fraction and its relationship



Figure 1. View of $(Si_2O_5)^{-2}$ Sheet. Large Spheres = Oxygen Ions; Small Spheres = Silicon Ions

to soil behavior. It is believed also that such a study will bring about a better understanding of the variables affecting soil behavior and will result in a more adequate definition and control of the properties of soil.

This paper is the first of a series reporting on investigations of the clay fraction in soils. The objectives of these studies are (1) to specify tools and methods suitable for engineering laboratory use by which the clay fraction may be analyzed; (2) to study the role of the clay fraction in soils to determine the variables involved and their influence on engineering properties; and (3) to obtain a basis upon which the analytical results may be applied to determine and control the engineering behavior of soils.

Part I of this series describes the differential thermal method of analysis. This is a rapid, relatively accurate means for analyzing engineering soils qualitatively for certain constituents, particularly the clay minerals. The emphasis, however, is not on the method in itself but rather on procedures of sample preparation by which the sensitivity and usefulness of the method may be greatly increased and on the interpretation of patterns obtained from these samples.

STRUCTURE OF THE CLAY MINERALS

In order to understand the properties and methods of analysis of the clay fraction, some knowledge of the chemical and structural make-up of the major clay minerals is essential. The clay minerals which predominate in engineering soils may be classified in three groups, the kaolinite group, the montmorillonite group, and the illite group. The basic structural unit of all the minerals in the three groups is the silicon-oxygen sheet having the formula (Si₂O₅)⁻². Each silicon ion is surrounded by four oxygen ions and each group shares three of the four oxygen ions with its neighboring groups. Figure 1 shows a perspective view, exploded in the vertical direction of the spatial arrangement of the oxygen and silicon ions. The valence requirements of the oxygen ion situated directly above the silicon ion are unsatisfied and it is available to other ions for bonding.

The only mineral of the kaolinite group which occurs in any abundance is the parent mineral kaolinite; nacrite and dickite are scarce and differ from kaolinite only in minor structural features. All forms have the composition $(OH)_4Al_2Si_2O_5$. The structure of this mineral may be thought of as consisting of one basic silica sheet, as described in the preceding paragraph, with the aluminum ions bonded to the unsatisfied oxygens. Since each aluminum ion must be surrounded by six negative ions, hydroxyl ions, $(OH)^-$, are necessary to complete the structure and to satisfy all the valence requirements.

The basic formula for the minerals of the montmorillonite group is $(OH)_2Al_2(Si_2O_5)_2$. This may be considered as being composed of two silica $(Si_2O_5)^{-2}$ sheets joined together by aluminum ions, with the hydroxyl ions again being present to complete the structure. However, the actual chemical compositions of the minerals of this group vary considerably, owing to the possibility of such ions as iron and magnesium acting with the aluminum ions and partially replacing them for the bonding together of the silicon-oxygen layers. The nature of the mineral is such that it may take up considerable water between the platey particles and thereby swell markedly.

The illite group of minerals has approximately the same basic formula as the montmorillonites. However, in this group some of the silicon ions in the basic sheet have been replaced by aluminum ions. This gives rise to a deficiency in charge which is made up by the inclusion of potassium ions between the particle lavers. These potassium ions are actually bonded to adjacent particles and tend to restrict the movement of the sheets. The formula for this group may be expressed as $K_{y}(OH)_{2}Al_{2+y}Si_{4-y}O_{10}$, the value of y varying from .25 to .75. Again, as with the montmorillonites, the aluminum ions are partially replaced by iron and magnesium ions. Water is also taken up between the particles, but swelling is limited by the presence of the potassium ions.

DIFFERENTIAL THERMAL ANALYSIS

The differential thermal method of analysis has as its basis the heat effects accompanying the reactions which occur in a substance upon heating. When a material is heated, it may undergo one or more reactions which either give off heat (exothermic) or absorb heat (endothermic). A common example of an exothermic reaction is the burning of organic matter upon heating; an illustration of an endothermic reaction is the break-down of CaCO₃ into CaO (lime) and CO₂. Many minerals undergo characteristic reactions, such as loss of water, break-down of the crystal structure, mineral inversion, crystallization, etc., at known temperatures, and these reactions form the basis for their identification. The differential thermal analysis utilizes this fact by comparing the temperature of the sample with that of an inert standard while the two materials are being heated through a given temperature range, usually 50 to 1000 deg. C. Since the temperature at which these reactions occur varies with the rate of heating, a constant rate, generally 10 to 12 deg. C. per min., is used. This enables one to utilize standard thermal curves to interpret the results.

The apparatus employed to obtain the test curves consists of a furnace with adequate control to give the proper heating rate, a

temperature measuring unit, and a means of determining the differential between the sample and standard. A number of workers have presented descriptions of various types of apparatus. Some of these are given in the references listed at the end of this paper.

The apparatus used in this work was designed and built in the Ceramic Engineering



Figure 2. Thermal Analysis Apparatus







laboratory at Iowa State College. It is so constructed that it can be operated fully automatically or manually. The furnace is heated by Kanthal wire wound around an alumina tube. The temperature is controlled for automatic operation by a Bailey Pyrotron controller recorder; manual control is by means of a Variac in the furnace circuit. The temperature difference between sample and standard is determined by the use of a differential thermocouple, which is essentially two thermocouples joined so as to have opposing electromotive forces. The junctions of this couple are set in the middle of two holes in a nickel block. These holes serve as the holders for the sample and standard which are packed carefully around the thermocouple wires. Figure 3 shows in detail the construction of this unit. Any temperature difference between the sample and standard gives a resulting e.m. f., the magnitude of which is proportional to the temperature difference and the direction of which is dependent upon the relative temperatures. The leads from the differential thermocouple are connected to a galvanometer through a variable resistance. The deflection of the galvanometer is recorded on photographic paper by reflecting a light beam from a mirror mounted on the galvanometer suspension, thereby recording the thermal curve. A means is also provided to mark the curve at 50 deg. C. intervals.

The sensitivity of the apparatus is controlled by the variable resistance in series with the galvanometer. Some reactions are accompanied by a relatively large heat effect and require only moderate sensitivity, whereas for others a very sensitive apparatus is needed for detection. The ultimate sensitivity is limited principally by the ambient effect of the furnace heating as reflected in the temperature at the center of the samples due to the difference in thermal conductivity of the sample and standard. This effect may be controlled somewhat by using, as a standard, sample material which has been subjected to previous heat treatment, and by packing both the sample and standard to approximately the same density. In order to compare the thermal curves obtained from different samples, a uniform amount of material should be used.

SAMPLE PREPARATION

For analyses of relatively pure minerals or of a mixture which contains the mineral of interest as a major component, little or no sample preparation is needed. However, to investigate minor constituents, it may be necessary to treat the sample in such a manner as to increase the relative amount present or to remove those components whose heat effects may interfere with the desired reaction. The absolute percentage of a mineral which will give an interpretable reaction depends upon the amount of heat released or absorbed by the reaction and, therefore, that percentage is different for each substance, the actual minimum being determined only by experimentation.

Since the clay fraction in some engineering soils occurs in amounts too small to give a definite characteristic pattern, one of the major objectives of this work is to present a rapid method for increasing the concentration of the clay fraction and to illustrate how this

method may be applied to certain soils. For this purpose seven soils were used. They are designated descriptively as: (1) Harrison County loess, (2) Johnson County loess, (3) Edina subsoil, (4) Kansan gumbotil, (5) Maryland soil-aggregate, (6) synthetic soil, and (7) Webster topsoil.

The Harrison County loess is thought to be of eolian origin and was obtained from the deep Peorian loess area bordering the floodplain of the Missouri River in western Iowa. The sampling pit was near the bottom of a 60-ft. road cut about 4 mi. west of the town of Magnolia. This silty loam material had a light grayish-yellow color and classified A-4(8) by the revised Public Roads classification system.

The Johnson County loess, also of Peorian sub-age, was sampled about 7 ft. from the top of a road cut near Iowa City in eastern Iowa. The sample had a reddish-yellow color and a silty clay loam texture. It classified A-7-6(10).

The sample of Edina subsoil was taken from a roadside pit near the town of Corydon in Wayne County, southern Iowa. This dull gray B horizon soil had a clay texture and classified A-7-6(20). The parent material (C horizon) of the Edina series is moderately deep to shallow loess.

The name "Kansan gumbotil" has been applied to the highly weathered grayish material derived from and overlying Kansan glacial till. The sample used was obtained from a surface exposure near the town of Corydon, Iowa. It had a clay texture and classified A-7-6(19).

The soil designated Maryland soil-aggregate¹ was rust-red in color and was obtained from a small pit in Prince George's County, Maryland, about $4\frac{1}{2}$ mi. south of the District of Columbia line just off the road to Indian Head, Maryland. Texturally it classified as gravelly sandy loam and by the revised Public Roads system as A-2-6.

In connection with previous work at the Iowa Engineering Experiment Station, a synthetic soil had been prepared. The non-clay portion of the soil was Ottawa sand and the clay fraction Florida kaolin. This sample was used to illustrate the typical thermal reactions of a kaolinitic type soil. It classified texturally

¹Furnished by the Division of Physical Research of the Bureau of Public Roads. as sandy loam and A-2-4 by the revised Public Roads system.

The sample of Webster topsoil was taken from the A horizon of a corn field about 2 mi. north of the city of Ames in Story County, central Iowa. It had a high organic matter content and a silty clay loam texture. It classified A-7-6(13). The parent material of the Webster series is Wisconsin (Mankota sub-age) till.

Thermal patterns were made for the following fractions of each of the soils listed above: (1) the entire soil, (2) that portion which passed a 270-mesh sieve, and (3) the minusone-micron fraction. For the samples indicated as (1) the soil was ground to pass a 40-mesh sieve. For the other two samples 100 g. of the soil to be tested was mixed with about 700 ml. of distilled water, and sufficient sodium silicate² was added to disperse the clay. The dispersed soil is then passed through a 270mesh sieve and the residue discarded. For the minus-270-mesh fraction, the suspension is acidified with a few drops of hydrochloric acid. This causes the clay to flocculate, or form large aggregates, and the solids settle rapidly. In this work, the rate of settling was accelerated by the use of a centrifuge, the entire settling taking only a few minutes.

For the finest fraction, the suspension obtained by sieving is allowed to settle, and the less-than-1- μ sample is siphoned off. The length of time settled and the amount of suspension siphoned off may be determined from Stokes' Law, governing the velocity at which a spherical body falls through a liquid. This may be written as:

$$v = \frac{2r^2 g(S_s - S_l)}{9_n}$$
 (1)

where: v = velocity of settling in cm. per sec.

r = radius of the particle in cm.

² The amount of Na_2SiO_3 used depends on the type and amount of the clay fraction and is most easily determined by visual inspection. A properly deflocculated suspension has a uniform, fine-grained appearance as contrasted to the coarse appearance and rapid settling of an undispersed system. This contrast is readily observed, especially if a few drops of acid are added to another sample for comparison. A few experiments of this type should enable a person inexperienced in this field to recognize the desired state.

- g = acceleration of gravity, 980 cm.per sec.²
- S_s = specific gravity of the solid, averaging about 2.58 for clays
- S_i = specific gravity of the water, roughly equal to 1
- $\eta =$ viscosity of the water, equal to approximately .01 poises.

The values given above are only approximations; accurate values for water may be determined from any chemistry or physics handbook and vary with temperature. However, these values are accurate enough to give an indication of the time interval involved. The distance settled l in an interval of time



Figure 4. Thermal Curves of Webster Topsoil

for $1-\mu$ diameter particles may be calculated as follows:

$$v = \frac{l}{t} = \frac{2 \times .00005^2 \times 980 \times (2.5 - 1)}{9 \times .01}$$

$$v = 8.175 \times 10^{-5} \text{ cm. per sec.}$$

$$= .2943 \text{ cm. per hr.} (2)$$

From equation (2) it may be calculated that a 1- μ diameter particle would settle approximately 7 cm. in 24 hr. Since the long-arm centrifuge employed by the authors in these experiments is capable of developing a centrifugal acceleration of 220 times gravity, its use enabled the settling of 1- μ particles a distance of 5 cm. in approximately 44 min. This made it possible to siphon off the top 5 cm., add water and re-mix, and repeat until sufficient amount of sample has been obtained. This procedure greatly decreases the time necessary for sample preparation.

The suspension containing the minus- $1-\mu$ fraction is removed and acidified and allowed to settle, as is done with the fraction which

passes the 270-mesh sieve. After settling, most of the supernatant liquid is poured off, and the remaining water is removed by filtering in a Beuchner vacuum filter. The resulting filter cake is air-dried in an air blast. The reason for filtering and air-drying is to preserve the reaction which occurs in the illite and montmorillonite minerals between 100 and 250 deg. C.



Figure 5. Thermal Curves of Samples of Montmorillonite, by Grim and Rowland (13)

Oven drying, although at a temperature only slightly above 100 deg. C, will remove the major portion of this reaction. An illustration of the difference in the types of curves obtained may be seen in Figure 7, curves 2a and 2b. Curve 2a was obtained from an oven-dried sample, curve 2b from an air-dried sample.

Sometimes in addition to increasing the concentration of the clay fraction it is necessary to remove constituents whose reactions tend to obscure the reactions which are desired. Organic material is particularly troublesome in this respect, since its reaction with oxygen causes large exothermic effects over almost the entire temperature range, and since it is so widespread in certain types of soils. Figure 4, curve 1, indicates the interference caused by organic material. Such material may be removed by treating the sample with



Figure 6. Thermal Curves of Samples of Illite, by Grim and Rowland (13)



Figure 7. Thermal Curves of Harrison County Loess

hydrogen peroxide until no further reaction occurs. Cautious heating may be employed to hasten the reaction, but care should be taken that the evolved CO_2 does not cause the sample to froth over the container. The amount of H_2O_2 necessary depends on the sample and often the removal of the organic material is time consuming and laborious. However, when it has been completed, excellent patterns may be obtained on the sample, as is shown by curve 2, Figure 4. Although a small amount of certain types of organic matter may be removed in the preparation of the less-than- $1-\mu$ sample as shown in Figure 9, this did not suffice for the organic content of Webster topsoil.

Another group of interfering minerals which may be present are the carbonates, which give endothermic reactions between 750 and 900 deg. C. However, these may be easily removed by the addition of a few drops of hydrochloric acid. In curves 1 and 2a of Figure 7 is shown the typical carbonate reaction. This reaction, however, is absent from curves 2b and 3, since the sample preparation included the addition of acid. If the presence of the carbonates, limestone, dolomite, etc., is of importance, as it usually is in engineering soil studies, a pattern should be taken on untreated material as well as the acid-treated.

INTERPRETATION OF ANALYTICAL RESULTS

Interpretations of the thermal curves obtained are based upon the pure mineral curves presented by Grim and Rowland (13). Since the pattern for kaolinite is very distinctive, the curve obtained from the synthetic soil (quartz plus Florida kaolin) will serve to illustrate the characteristic reactions of this mineral. This is given in Figure 12, curve 3, and shows a strong endothermic reaction centered between 550 and 600 deg. C. and a sharp exothermic peak at 980 deg. C. However, the patterns obtained from montmorillonite and illite are quite similar. Figures 5 and 6 show the patterns obtained by Grim and Rowland on pure samples, the mineralogical contents of which have been determined by X-ray methods. It will be noted that both minerals give three endothermic and one exothermic reaction. Only the second endothermic reaction may be used as a basis for differentiation. This occurs between 500 and 600 deg. C. in the case of the illites, and between 600 and 700 deg. C. for the montmorillonites. An inspection of the curves of Figures 5 and 6 will show that this is true for each sample presented. It is upon these curves that the authors have based their interpretations of the soil analyses to be presented.

Figures 7 through 12 present the patterns of the various samples studied. In each figure the individual curves are numbered 1, 2, and 3; these designate the original, through-270-mesh, and less-than-1- μ samples respectively.

Figure 7 contains the analyses of Harrison County loess. Curve 1 shows the presence of quartz (endothermic at 573 deg. C.) and car-



Figure 8. Thermal Curves of Johnson County Loess





Figure 10. Thermal Curves of Kansan Gumbotil

bonates (double endothermic reaction, 800 to 900 deg. C.). The curves 2a and 2b were both made from the through-270-mesh sample; however, curve 2b shows the analysis of an acid treated, air-dried sample, and curve 2a is of a heat-dried sample. Although heat drying preserved the carbonate reaction, the loss of the low temperature endothermic reaction greatly reduced the value of the pattern for clay mineral determination. Curve 2b presents the typical illite pattern, and this is further confirmed by curve 3. It will be noted that the major portion of the quartz present in the soil was above 1 μ since the quartz reaction does not appear in curve 3.



Figure 11. Thermal Curves of Maryland Soil-aggregate



Figure 12. Thermal Curves of Synthetic Soil (Sand and Kaolin)

The Johnson County loess, shown in Figure 8, gives the typical illite reaction on all three samples. The curves also indicate that most of the sample is below 270-mesh size, since there is little increase in reaction magnitude between curves 1 and 2. This soil also contains quartz, as is readily evident by the 573 deg. C. reaction (high-low quartz transformation).

Figure 9 contains the thermal patterns of the Edina subsoil. This soil contains a large amount of clay fraction which is predominately illite. The broad exothermic reaction from 250 to 550 deg. C. is caused by the presence of some organic material. This reaction tends to partially mask the illite endothermic reaction at 550 to 600 deg. C. No good evidence for the presence of quartz is indicated, since the sharp point at about 575 deg. C. may be caused by the combination of the reactions of the organic material and the illite.

Kansan gumbotil offers a series of interesting patterns, as given in Figure 10. The pres-



Figure 13. Thermal Curves of Prepared Mixtures of Illite and Montmorillonite, by Grim and Rowland (13)

ence of quartz is observable in curves 1 and 2. An examination of the standards of Grim and Rowland, Figures 5 and 6, shows that the only samples exhibiting a double initial endothermic reaction are included in Figure 5, that of the montmorillonites. No explanation of this behavior has been given by Grim or other workers; and, since it does not occur in all montmorillonite samples, it is the opinion of the authors that the position of the second endothermic peak, between 500 and 600 deg. C., should constitute the major basis for analysis. On these grounds, the clay fraction must be classified as an illite.

Figure 11, the Maryland soil-aggregate sample, offers an example of a soil with a very large amount of coarse quartz and very little clay. However, comparison of curves 1 and 2 indicates that the major portion of the nonclay fraction is above the 270-mesh sample, curve 2.

As stated, the patterns shown in Figure 12 were obtained from samples of a synthetic soil composed of sand and kaolin. The presence of the quartz sand is readily evident from the strong, sharp endothermic reaction at 573 deg. C. in curves 1 and 2. Curve 1 shows only a trace of the exothermic reaction at 980 deg. C. which is distinctive of the mineral kaolinite. It is interesting to note that the amount of clay in this soil was approximately five percent; therefore this seems to be the minimum amount which could be identified by this method. The kaolinite reactions become more pronounced in curve 2, and curve 3 shows clearly the characteristic reaction at 980 deg. C.

A close examination of the patterns for the Harrison County loess (Fig. 7) and Edina subsoil (Fig. 9) reveals that a slight tendency toward an endothermic reaction exists between 650 and 700 deg. C. This might be interpreted as being caused by a small amount of montmorillonite. Figure 13 presents the patterns obtained by Grim and Rowland (13) on prepared mixtures of illite and montmorillonite. A comparison between the Figures 7 and 9 and Figure 13 indicates that, if it is present, montmorillonite occurs as less than five percent of the minus-1-µ fraction. Assuming a clay content of 20 percent, the amount of montmorillonite present would be less than one percent of the total soil. Similarly, since approximately five percent is the observable minimum for the mineral kaolinite and no typical 980 deg. C. exothermic reaction was observed on the soils studied, it may be stated that if kaolinite is present, it occurs in amounts less than one percent of the total soil.

An interesting comparison may be made between the thermal patterns obtained on the original samples and the revised Public Roads classification. All soils having a classification of A-7-6, denoting high plasticity, gave an interpretable pattern without treatment. These soils were Johnson County loess (Fig. 8), Edina subsoil (Fig. 9) and Kansan gumbotil (Fig. 10). The remaining soils, Maryland soil-aggregate (Fig. 11), Harrison County loess (Fig. 7), and the synthetic soil (Fig. 12), all required preparation of the soil to increase the clay concentration, and all have a low plasticity classification.

CONCLUSIONS

From the work described above it may be concluded that:

1. The mineralogical analysis of the clay fraction of soils by the differential thermal method may be greatly aided by proper preparation of the sample.

2. For some soils containing small amounts of the clay minerals, identification by this method is not possible unless the soil is treated in such a manner as to increase the clay concentration in the sample.

3. Some materials, such as organic matter, whose reactions are objectionable in that they obscure those of the minerals for which the soil is being analysed, may be removed by the proper soil treatment.

4. The difference in the extent and intensity of the thermal reactions obtained on the prepared samples gives an estimation of the particle-size distribution in the soil.

5. The differential thermal method of analysis in conjunction with the proper soil preparation methods is a valuable tool for the analysis of the mineralogical content of soils and especially for the analysis of the basic clay content. However, the data obtained on the soil by this method constitute only a part of that necessary for the complete analysis. Therefore its value is greatly increased by such complementary data as accurate particle-size distribution and cation exchange capacity.

At the present time, perhaps the greatest lack in the data obtainable on soil samples, and on the clay fraction in particular, is in a clear, concise application of this data to the determination and control of the engineering properties of the soils. It is toward this end that the authors have begun the series of studies of which this is the first.

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PART II-DISTRIBUTION AND CATION EXCHANGE CAPACITY

Since the clay minerals in a soil occur for the most part in the colloidal fraction of engineering soils, any attempt to rationalize the properties of the soil must be directed not at the chemical nature but rather at those properties of the soil which predominate in the colloidal realm. As a basis for rationalization it is necessary that the distribution of particle sizes existing in the soil as a whole be known, including those particles in the minus-one-micron¹ size range. Similarly, since the exchangeable cations associated with the soil have a profound effect on the colloidal behavior, a knowledge of the amount and type of exchangeable cations present is of great value.

Therefore, it is the opinion of the authors that any work dealing with the study of the properties of the clay minerals must necessarily include a discussion of these variables both with respect to simple, accurate determinative methods and, of more importance, to a correlation of the data so obtained with

¹ One micron $(1 \mu) = 0.001$ mm.

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some engineering properties of soils. At present a complete correlation is not possible due to the lack of sufficient data. However, a start may be made, and it is hoped that further studies will enable the soil engineer to utilize these tools more fully.

PARTICLE-SIZE DETERMINATION

The measurement of particle-size distribution in the colloidal range is a relatively recent development. The distribution of particles of microscopic size may be determined by counting techniques, but the procedure is tedious and time consuming, and the information so obtained is not sufficient to warrant its use to any extent. Several methods for determining the size of fine particles have been proposed which are based on Stokes' Law for spheres falling through a medium. By means of this equation,

$$\boldsymbol{v} = \frac{2r^2 g(S_s - S_l)}{9\eta} \tag{1}$$

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Since the clay minerals in a soil occur for the most part in the colloidal fraction of engineering soils, any attempt to rationalize the properties of the soil must be directed not at the chemical nature but rather at those properties of the soil which predominate in the colloidal realm. As a basis for rationalization it is necessary that the distribution of particle sizes existing in the soil as a whole be known, including those particles in the minus-one-micron¹ size range. Similarly, since the exchangeable cations associated with the soil have a profound effect on the colloidal behavior, a knowledge of the amount and type of exchangeable cations present is of great value.

Therefore, it is the opinion of the authors that any work dealing with the study of the properties of the clay minerals must necessarily include a discussion of these variables both with respect to simple, accurate determinative methods and, of more importance, to a correlation of the data so obtained with

¹ One micron $(1 \mu) = 0.001$ mm.

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some engineering properties of soils. At present a complete correlation is not possible due to the lack of sufficient data. However, a start may be made, and it is hoped that further studies will enable the soil engineer to utilize these tools more fully.

PARTICLE-SIZE DETERMINATION

The measurement of particle-size distribution in the colloidal range is a relatively recent development. The distribution of particles of microscopic size may be determined by counting techniques, but the procedure is tedious and time consuming, and the information so obtained is not sufficient to warrant its use to any extent. Several methods for determining the size of fine particles have been proposed which are based on Stokes' Law for spheres falling through a medium. By means of this equation,

$$\boldsymbol{v} = \frac{2r^2 g(S_s - S_l)}{9\eta} \tag{1}$$

- where: v = velocity of settling
 - r = radius of the particle settling
 - g = acceleration of gravity
 - S_s = density of the solid
 - $S_I = \text{density of the suspending me-}$ dium
 - η = viscosity of the suspending medium

it is possible to determine the rate of settling and from this the size of particles which have settled a given distance. The particle-size distribution may then be found by determining the actual amount of material at any given depth at different times. The amount of material may be found by taking a sample at the desired depth and weighing the dried solids, as in the Andreasen pipette method, or by measuring the specific gravity of the suspension at that depth. Although the former method is the more accurate, it is time-consuming. For this reason, a variation of the latter method has been adopted for this work. The procedure is patterned after that proposed by Norton and Speil (2) in which the specific gravity of the suspension is measured by a soil hydrometer (range of 1.010 to 0.990).

The suspension employed contains two percent solids by weight, i.e., 2 g. of clay per 100 cc. of water. The specific gravity measured is assumed to be that of the suspension at the center of the hydrometer bulb; therefore, the particle size being investigated is that size which has settled from the surface of the liquid to the center of the hydrometer bulb. The hydrometer reading is used to determine the percentage of solids finer than that size by means of the following equation:

 $W \text{ per cent} = \frac{S_s}{S_s - 1}$

$$\times \frac{100}{C} \left(S - S_l \right) \times 10^8 \quad (2)$$

Where: S_s = density of the solid

- S =specific gravity of the suspension
- S_i = specific gravity of the suspending medium
- C = concentration of the solid, g. per liter.

Since the immersion depth of the hydrometer is variable, depending on the specific gravity, the calculation of equivalent spherical diameter of the particle is greatly simplified by the use of the Casagrande nomographic charts.²

From equation (1), the velocity of settling decreases as the square of the radius of the particle, i.e., a given particle will settle only one-fourth as rapidly as a particle twice its size. Therefore, it is desirable to increase the settling rate of the particles in the finer size ranges by the use of a centrifuge. In this way, the acceleration of the particles is increased over that obtained by gravity settling. In order to apply Stokes' Law to centrifugal settling it is necessary to substitute the acceleration obtained for the acceleration of gravity g in equation (1). This is calculated as follows:

$$\alpha = r\omega^2 \tag{3}$$

where: α = acceleration

r = radius of circle of revolution

 $\omega =$ angular velocity

The centrifuge used in this study is shown in Figure 1 and is capable of developing an acceleration of 225 times gravity.



Figure 1. Long-arm Centrifuge

The data obtained from equations (1) and (2) are plotted on semilog paper with the weight percent finer versus the logarithm of the particle size (as shown in Figs. 2 and 3). The particle size distribution may be read directly from the graph in the form of the weight percentage of soil particles whose diameters are less than any given size. The distribution may also be expressed in terms of the percent of the soil particles existing in a

² These charts may be obtained from the Soil Mechanics Laboratory, Massachusetts Institute of Technology, Cambridge, Mass. series of size ranges, e.g., clay (less than 5 μ), silt (5 to 50 μ), and sand (greater than 50 μ). In the measurement of particle size by set-

the measurement of particle size by settling rates, perhaps the most important single the soil was accomplished by the addition of sodium silicate, the optimum amount being determined by settling tests. A series of suspensions containing varying amounts of elec-



consideration is the dispersion of the solid into individual particles. Solids in the finer size range have a marked tendency to agglomerate unless the proper sample preparation is made. For the work described herein, dispersion of trolyte were made up and allowed to stand for several hours. The optimum amount of electrolyte was found by visual inspection of the suspensions, the best deflocculated having the smallest clear layer at the top and the least amount of solids settled out at the bottom. After the proper amount of electrolyte had been added, the soil sample being prepared for analysis was tumbled end over end for at least 3 days. The dispersion was then checked by microscopic examination.

CATION EXCHANGE CAPACITY

One of the most important properties of a clay mineral is its cation exchange capacity. This property is closely connected to the physical behavior of the mineral, for example its plasticity and shrinkage. In addition, a knowledge of the cation exchange capacity of the mineral or soil is necessary for proper treatment of engineering soils, e.g. stabilization by organic cations.

The exchange capacity values vary widely depending upon the type and particle size of the clay mineral involved. In general, it may be said that these values, expressed as milliequivalents of cation per 100 g. of soil, are 85-100 for montmorillonite, 25-60 for illite, and 3-15 for kaolinite.

It is thought that the clay minerals adsorb cations by one or both of two different mechanisms. The first is the attraction of cations to the edges of the broken clay particle. It is known that the clay particles occur mainly in the finest size range, and in this range the area of the broken edges becomes significantly large. Also as the size of the particles decreases. the edge area per unit mass increases. The atoms occurring at the particle edge possess unsatisfied bonds, and it is by these bonds that the cations are attracted to the particle. A detailed description of the adsorption process and its modifications is beyond the scope of this presentation. Many excellent treatises have been published concerning this subject, and some of these are listed in the references.

The second mechanism by means of which cations are held to the clay particle is the result of substitution of such ions as iron and magnesium for aluminum in the crystal lattice. Since ferrous iron and magnesium are both divalent, the substitution of these for trivalent aluminum gives rise to a deficiency of positive charge in the structure. This deficiency may be satisfied by cations which do not become an integral part of the lattice but are nevertheless strongly attracted or adsorbed to the particles. As would be expected from the structures of the clay minerals (see Part I of this series), this second mechanism is operative only in the montmorillonites and illites, whereas the adsorption of ions to the broken edges takes place both in these minerals and on kaolinite.

The adsorbed cations are attracted to the particle more or less strongly depending upon the ion involved. The higher the charge on the cation the stronger is the attractive force, calcium being more tightly held than sodium. For ions of constant charge the force of attraction also varies and is believed by some to be dependent upon the degree of hydration of the ion. The cation hydrogen is anomalous in its behavior and is more tightly held than any other cation.

When an electrolyte is added to a clay, the cation of the electrolyte tends to replace the cation adsorbed on the clay particle to a greater or lesser extent depending upon their relative valencies, their degree of hydration, their respective concentrations, and the degree of solubility of the chemical compound formed. For example, when a clay containing adsorbed calcium cations is treated with sodium chloride, the following chemical reaction occurs:

$$\begin{array}{l} \text{Clay-Ca + NaCl} \\ \rightleftharpoons \text{Clay-2Na + CaCl}_2 \end{array} \tag{4}$$

The equilibrium established will tend to favor the calcium clay since the calcium ion is more strongly attracted by the clay than the sodium and since (calcium chloride being soluble) no calcium ions will be removed from the solution. However if this same clay is treated with sodium silicate, the reaction will occur as follows:

$$\begin{array}{c} \text{Clay-Ca + Na_2SiO_3} \\ \rightleftharpoons \text{Clay-2Na + CaSiO_3} \end{array} \tag{5}$$

This reaction differs from that above in that one of the products is relatively insoluble calcium silicate. Therefore any calcium ions replaced by sodium will be removed immediately from the solution in the form of calcium silicate and the reaction will progress to the right, forming a sodium clay.

The total amount of exchangeable cations associated with the soil available for exchange reactions such as those described above, may be divided into two classes, the exchangeable bases such as sodium and calcium, and exchangeable hydrogen. This division arises from the fact that for most experimental methods for determining the amount of cation associated with a clay (the cation exchange capacity) these two quantities are determined separately. This is true for the method employed for this study. Numerous methods for determining both base and hydrogen-ion exchange capacity have been presented in the literature. The method originated by Brown (5) is described below and was selected by the authors because of its speed and because of the simplicity of the technique and of the equipment required. The equipment needed for this de-



Figure 4. Potentiometric Titration of Normal Ammonium Acetate



Figure 5. Potentiometric Titration of Normal Acetic Acid

termination is a pH meter capable of measuring pH to .02 pH units, neutral normal ammonium acetate, and 1 normal acetic acid. The procedure as given by Brown is as follows:

"To determine exchangeable hydrogen, 2.5 g. of soil is placed in a 50 ml. Erlenmeyer flask, 25 ml. of neutral normal ammonium acetate is added, the flask is stoppered, and the 1 to 10 mixture is allowed to stand for 1 hr. with occasional shaking. The pH is determined on the mixture. To determine total exchangeable bases, 2.5 g. of soil and 25 ml. of normal acetic acid are mixed and treated in the same manner as the mixture prepared for exchangeable hydrogen determination. The pH of the mixture is determined."

The number of milliequivalents of exchangeable hydrogen and exchangeable bases are found from Figures 4 and 5 respectively. Figure 4 was obtained by potentiometric titration of 100 ml. of neutral normal ammonium acetate buffer with 0.2 N acetic acid. The number of milliequivalents resulting in a given pH value is then multiplied by 10 so as to express the results in the units of milliequivalents per 100 g. of clay, the usual manner of expressing exchange capacity. The factor of 10 is necessary, since a soil-buffer ratio of 1 to 10, as selected by Brown, would require 1000 ml. of buffer solution for 100 g. of soil. Since only 100 ml. of buffer solution is employed for the standard curves, the results must be increased tenfold to give the total milliequivalents for 1000 ml. of buffer. Figure 5 is obtained in a like manner by titrating normal acetic acid with 0.2 normal ammonium hydroxide.

This method was employed to determine the exchangeable hydrogen and exchangeable bases on samples of two Iowa soils: Harrison County loess and Johnson County loess³. Determinations of cation exchange capacities were also made on the minus-1-µ fraction. The separation of these samples was accomplished by settling methods. In order to decrease the time necessary for settling, the samples were treated with hydrochloric acid and then washed with distilled water to remove the excess acid, the hydrogen ions partially replacing the bases on the soil in the process. The results obtained from these tests are presented in Table 1. Also included in Table 1 are results obtained on the same soils

^a The Harrison County loess is thought to be of eolian origin obtained from the deep Peorian loess area bordering the flood-plain of the Missouri River in western Iowa. The sampling pit was near the bottom of a 60-ft. road cut about 4 mi. west of the town of Magnolia. This silty loam material had a light grayish-yellow color and classified A-4(8) by the revised Public Roads classification system. The Johnson County loess, also of Peorian sub-age, was sampled about 7 ft. from the top of a road cut near Iowa City in eastern Iowa. The sample had a reddish-yellow color and a silty clay loam texture. It classified A-7-6(10). by P. K. Fung (8) using the calcium oxalate method.

DISCUSSION OF RESULTS

The results obtained from the particle size distribution determination, as shown in Figures 2 and 3, indicate that the Johnson County loess contains a considerably larger amount of finer material than the Harrison County loess. and that the lower limit of particle sizes for the latter soil occurs at 0.1 μ , whereas for the former soil the particle sizes extend below this point.

The method for determining cation exchange capacity, as presented by Brown, was modified for certain phases of this investigation. Discussion of the modifications and of certain limitations encountered is therefore necessary. The standard titration curves given in the original article covered only the range 0-15 milliequivalents per 100 g. of soil; similar standard curves were prepared extending to 60 m.e. Figure 4, the titration of neutral normal ammonium acetate with approximately 0.2 normal acetic acid, shows that because of the changing slope of the curve the useful range is limited to less than 20 m.e. Of course this is an arbitrary limit which is set only by the degree of accuracy desired for the results.

To illustrate: assuming an accuracy of .02 in the pH measurements, the degree of error is 0.4 m.e. at 2 m.e. and about 2 m.e. at 35 m.e. A portion of this error occurring in testing soil having a high exchange capacity may be eliminated by using a different ratio of soil to buffer. Since the curve is based on a ratio of 1 to 10, the results obtained on a mixture of 1 part of soil per 20 parts of buffer, when multiplied by two, would give the capacity in terms of m.e. per 100 g. of soil. Experimental proof of this relationship is shown in the values obtained on Johnson County loess, a value of 42.5 m.e. resulting from a mixture of 1 part of soil to 10 parts ammonium acetate, and a value of 43.4 being obtained by doubling the results obtained with a 1 to 20 mixture. Therefore, Figure 5, the titration of 1 normal acetic acid with 0.2 normal ammonium hydroxide, covers only the range of 0 to 20 m.e. Values exceeding 20 m.e. may be obtained by the method described above.

One limitation of the cation exchange capacity method presented lies in its failure in soils such as Harrison County loess containing a high percentage of carbonate minerals. The initial results determined on this soil by the usual procedure were obviously in error since the pH of the ammonium acetate leachate actually increased slightly and the determination on the acetic acid leachate gave a result exceeding 100 m.e. Therefore the soil was treated with dilute hydrochloric acid to remove the carbonates and then washed with distilled water in a vacuum filter to remove the excess acid. After acid treatment, the total

TABLE 1 CATION EXCHANGE CAPACITIES, m.e. per 100 g.

Soil Sample	Ex- change- able Bases	Ex- change- able Hydro- gen	Total Ex- change- able Cations	Calcium Oxalate Method ^a
Johnson County loess whole soil -1μ fraction	8.8 2.8	3.7 42.5 43.4 ^b	12.5 45.3 46.2	14.1 45-50
Harrison County loess whole soil	1.8 4.0	9.8. 43.0 ^b	11.6 47.0	11.5 45-50

^a Tests performed by P. K. Fung. ^b Values determined using a ratio of soil to buffer of 1 to 20.

TABLE 2 PROPERTIES OF TWO LOESS SAMPLES

Soil Properties	Harrison County Loess	Johnson County Loess
Liquid limit, % Plasticity index, % Shrinkage limit, % Shrinkage ratio Volumetric change, % Centrifuge moisture equivalent, %. Field moisture equivalent, % Public Roads classification	31.9 26.4 5.5 21.7 1.61 26.7 16.6 23.7 A-4(8)	33.8 21.3 12.5 14.8 52.5 20.9 31.5 A-7-6(10)

^a Tests performed by P. K. Fung using A. A. S. H. O procedures.

exchange capacity as determined by the method presented agreed closely with that obtained by P. K. Fung (see Table 1). As would be expected, this converted the major portion of the clay to a hydrogen clay, as may be seen by comparing the exchangeable hydrogen and exchangeable base values given in Table 1. The determination on the minus- $1-\mu$ samples also showed a high amount of exchangeable hydrogen because of its acid treatment during settling. It may be noted here that the differential thermal analysis method, presented in Part I of this series, is an excellent method for the detection of the presence of carbonates.

Table 2 gives certain properties of the two loess soils which are indicative of engineering behavior. Comparison of this data with Figures 2 and 3, showing particle size distributions, indicates that the soil containing the higher percentage of particles in the fine sizes exhibits higher plasticity values, greater shrinkage, and a greater affinity for water, as would be expected. Correlation with cation exchange values cannot be made at this time due to a lack of fundamental research in this field. Another factor undoubtedly influencing these properties is the presence of carbonate minerals. Again sufficient knowledge is not available to evaluate their influence accurately.

CONCLUSIONS

Perhaps the most important conclusion that may be derived from the study presented above is that relatively simple, accurate methods for the determination of particle-size distribution and cation exchange capacity are now available to the soil engineer; however, correlation of the results obtained by these methods with soil properties cannot be made at present because of the lack of basic knowledge in the fields of soil technology and engineering. Further studies with the purpose of making available the knowledge necessary for the fullest application of analytical research to practical engineering are in progress.

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