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Water-Sorption Characteristics of Clay Minerals

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WATER-SORPTION CHARACTERISTICS
OF CLAY MINERALS

W. Arthur White and Ernesto Pichler

ABSTRACT

This investigation was made in order to determine the water-sorption characteristics of clay and other mica minerals and to study the relation between such water sorption and the properties of soils and sediments that contain the clay minerals.

Samples of kaolinite, montmorillonite, mica, chlorite group, and sepiolite-attapulgite-palygorskite group were tested in a modified Enslin apparatus, and water sorption was read at increasing time intervals. Sorption curves were plotted as semilogarithmic graphs.

The data show that montmorillonite adsorbs more water than kaolinite, illite, and chlorite. The chlorites and illites have similar water-sorption properties. Mixtures of clay minerals and mixtures of clay minerals and sand tend to have water-sorption properties proportional to the percentage of clay mineral present.

INTRODUCTION

This investigation was undertaken in order to determine the water-sorption characteristics of clay minerals, metamorphic chlorites, and igneous and metamorphic micas, and to explore the relation between such characteristics and the properties that the minerals may contribute to soils and sediments.

Studies were made of water-sorption characteristics of clay minerals, chlorites, and micas, the effect that aggregate size has on the rate of water-sorption, the effect that one clay mineral in a mixture of clay minerals has on the water-sorption characteristics of the mixture, and the effect that sand has on the water-sorption characteristics of a clay mineral in a mixture of sand and that clay mineral. The finely ground micas and chlorite minerals were included in the study because they, as well as clay minerals, are likely to be found in glacial deposits and because their presence also contributes to the properties of glacial sediments and their soils.

Data from this investigation may help the soil and construction engineers and geologists working with earth materials to understand the properties which the clay minerals may give to soils and sediments.

The data suggest that there are variations in the water-sorption characteristics within a clay mineral group and between the various clay mineral groups; that the water-sorption characteristics may be proportional to the percentages of the clay minerals in mixtures or that one clay mineral may contribute more to the water-sorption characteristics of the mixture than the percentages would suggest; and that in sand and clay mixtures either sand or clay may act as a dilutant or that clay may contribute more to the water-sorption characteristics than its percentages would indicate.

Montmorillonite will adsorb more water than the other three common clay minerals - kaolinite, illite, and chlorite. The chlorites and illites are similar to

each other in water-sorption properties. A mixture of clay minerals tends to have water-sorption properties that are proportional to the percentages of clay minerals present. Mixtures of clay minerals and sand tend to have water-sorption properties proportional to the percentage of clay mineral present.

PROCEDURE

Material Used

Samples of the kaolinite, montmorillonite, mica, and chlorite groups and of the sepiolite-attapulgite-palygorskite group were used in determining the water-sorption characteristics of the clay mineral groups. The clay minerals and their sources are listed below:

Kaolinite Group

Kaolinite from Twiggs County, Georgia; well crystallized variety, little plasticity.

Kaolinite from Union County, Illinois; poorly crystallized variety, very plastic.

Halloysite from Eureka, Utah; the $2H_2O$ variety.

Halloysite from Lawrence County, Indiana; the $4H_2O$ variety.

Montmorillonite Group

Montmorillonite from Belle Fourche, South Dakota; sodium is exchangeable cation. It swells several times its volume in water and readily sets up into a gel.

Montmorillonite from Cheto, Arizona; low-iron montmorillonite with calcium the chief exchangeable cation.

Montmorillonite from Tatatila, Vera Cruz, Mexico; high-purity montmorillonite with very low-iron content, calcium the chief exchangeable cation.

Montmorillonite from Pontotoc, Mississippi; a high-iron montmorillonite with calcium and hydrogen the exchangeable cations.

Nontronite from Spokane, Washington; a species of montmorillonite that has lath- or ribbon-shaped particles. Much of the aluminum is replaced by iron in the octahedral layer and aluminum replaces some silicon in the tetrahedral layers. The exchangeable cation is chiefly calcium.

Hectorite from Hector, California; a species of montmorillonite that has magnesium and lithium replacing aluminum in the octahedral layer and fluorine replacing some of the (OH) (Ross and Hendricks, 1945, p. 27). The chief exchangeable cation is sodium.

Mica Group

Illite from Grundy County, Illinois; a low-potassium, high-H_2O mica that is intermixed with mixed-lattice clay mineral and montmorillonite. The chief exchangeable cations are calcium and hydrogen. The pH is sometimes as low as two.

Illite from Vermilion County, Illinois; calcium the chief exchangeable cation.

Minford Silt from Jackson County, Ohio; a mixture of illite and chlorite, the chief exchangeable cation is calcium.

Muscovite from India from the University of Illinois collection; a dioctahedral mica with aluminum in the octahedral layer.

Biotite from Bancroft, Ontario, Canada; a trioctahedral mica with iron and magnesium in the octahedral layer.

Lepidolite from Coolgardie, Western Australia; a trioctahedral mica with lithium and magnesium in the octahedral layer.

Chlorite Group

Repidolite from Macon, North Carolina; a medium-iron chlorite.

Chlorite from London County, Virginia.

Prochlorite from Chester, Vermont; a medium-iron chlorite that contains a little more aluminum than repidolite.

Clinochlorite from Brewster, New York; a low-iron chlorite.

Sepiolite-Attapulgite-Palygorskite Group

Attapulgite from Quincy, Florida.

Palygorskite from the Sahara, North Africa.

Sepiolite from Madagascar.

Apparatus

The original apparatus described by Enslin (1933) (fig. 1) consisted of two funnels connected by means of a U-shaped tube. One funnel had a three-way stopcock at its base with a graduated tube attached to the 90-degree opening of the stopcock, and the other funnel had a filter plate whose horizontal axis was on the same line as the axis of the graduated tube of the first funnel. The second funnel had a lid with a small hole for an air vent to reduce evaporation to a minimum. The amount of water taken up by the clay minerals was determined from readings taken from the graduated tube, which can be read to 0.20 ml.

The apparatus used for the tests described below has been slightly modified by omitting the air bubble outlet and by connecting the graduated tube to the three-way connection by means of a rubber hose. Also, the diameter of the filter plate was only one inch, but that of the original was about two inches.
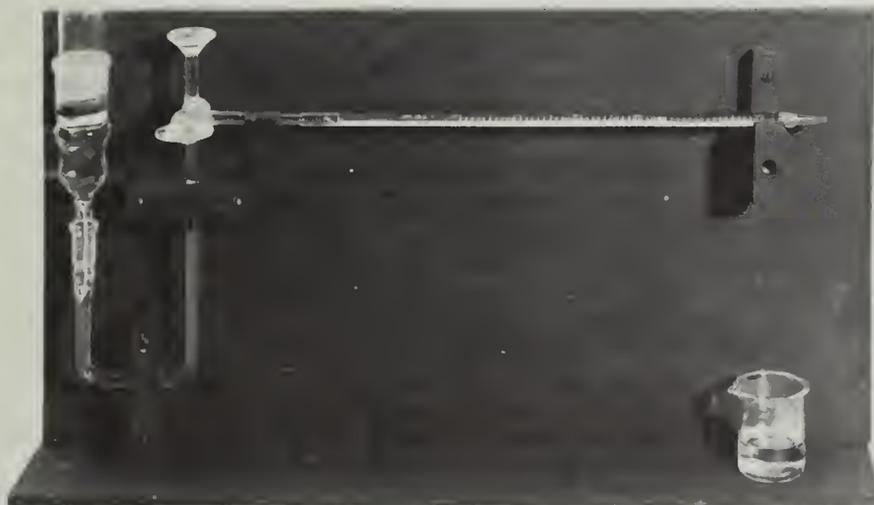

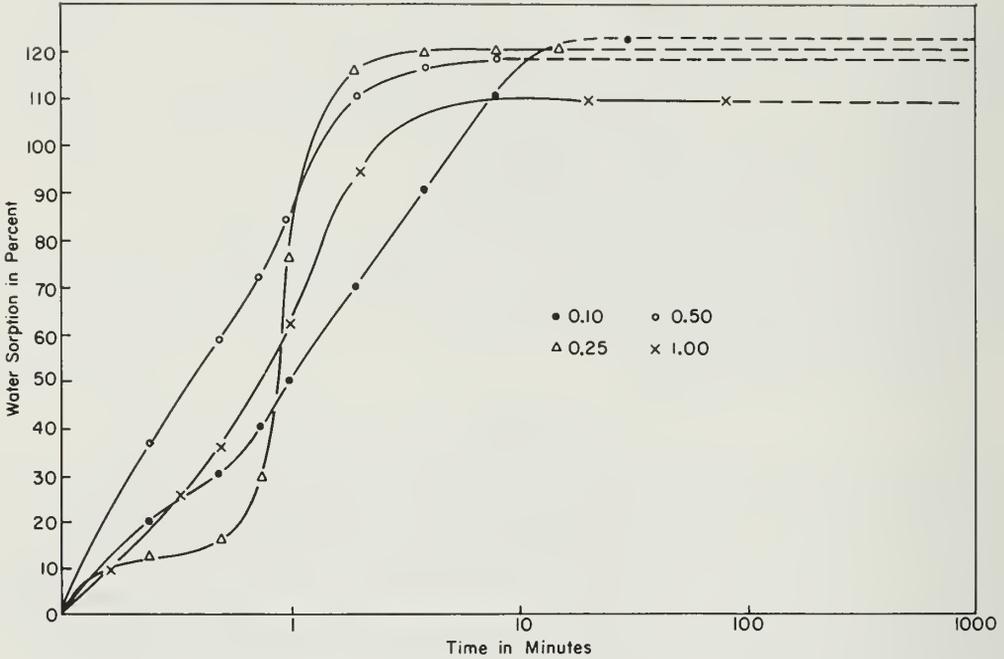Fig. 1. - Enslin water sorption apparatus.

Fig. 2. – Water-sorption curves for samples of various weights.

Test Method

To make the tests a weighed amount of material was placed on the filter plate, the bottom of which was in contact with the water surface, and the amount of water sorption was read at increasing time intervals. In order to find the quantity of material to be used, a number of tests were run using the same material under identical conditions and with quantities that ranged from 0.1 to 1 gram (fig. 2). Because it was found that 0.5 g. (corresponding approximately to 0.1 g. cm.^{2}) would give an average result, this amount was used throughout the test series.

The question of grain size of the material was also taken into consideration and investigated first, and then material with grain size less than 200-mesh was used for the rest of the experiment. The material was air-dried, and its moisture content was determined at the moment it was placed on the filter plate in order to permit the calculation of the percentage of water taken up with reference to the dry weight of the material. The sorption curves are plotted as semilogarithmic graphs, time along the logarithmic (abscissa) scale and the adsorbed moisture along the arithmetic (ordinate) scale. The possibility of evaporation influence on the readings was considered, but a number of tests showed that this influence may be neglected for test periods less than 1000 minutes. For tests longer than 1000 minutes, corrections were made for evaporation.
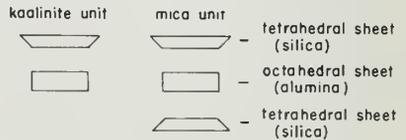

Fig. 3. – Schematic drawing showing the basic molecular layers in the unit cells of clay minerals. The trapezoid and rectangle represent the kaolinite type structure. The two trapezoids and one rectangle represent the mica type structure.
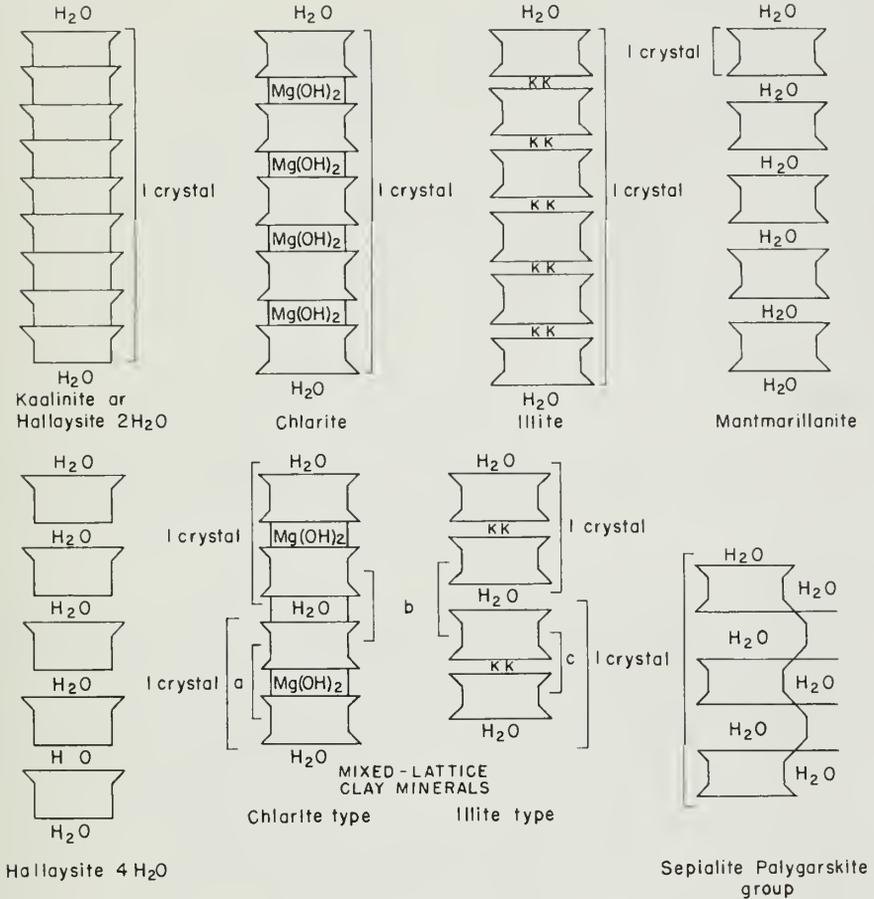
Fig. 4. - Schematic drawings of the structures of clay minerals
showing how the basic cells are bonded together.

H_2O = water $Mg(OH)_2$ = brucite sheet   K = potassium

a = part of crystal which has the properties of chlorite
b = part of crystal which has the properties of montmorillonite
c = part of crystal which has the properties of illite

DATA AND DISCUSSION

Clay Minerals

In order to understand the properties that clay minerals give to sediments, it is necessary to understand the structure of clay minerals. Figure 3 shows the two basic building blocks - units made of silica (or tetrahedral sheets) and alumina (or octahedral sheets) - which can extend indefinitely in two directions (except for the sepiolite-palygorskite group), but have a definite thickness in the third. Figure 4 shows how these basic building blocks are bonded together to build up the clay mineral crystals.
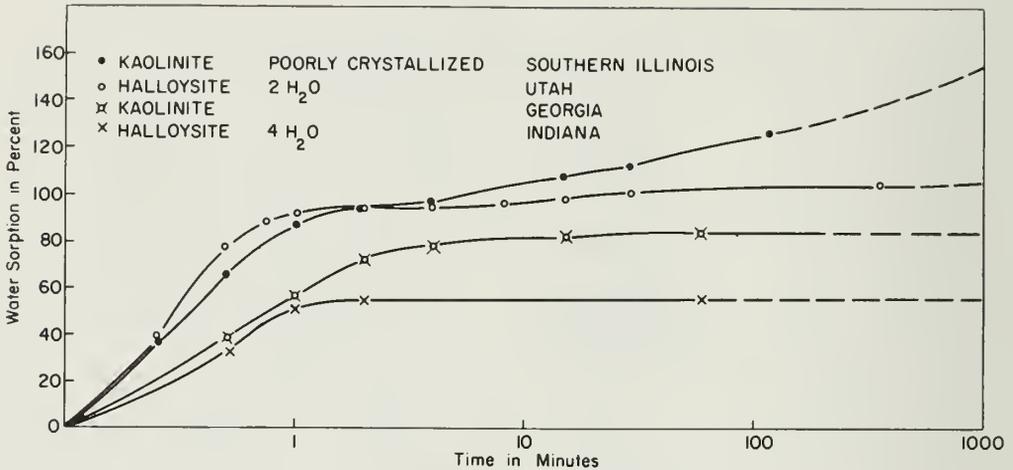
Fig. 5. – Water-sorption curves for the kaolinite and halloysite groups of clay minerals.

Kaolinite Group

Kaolinite crystallites (fig. 4) are composed of basic silicate layers (fig. 3), each of which consists of a silica sheet and an alumina sheet, and these basic layers are bonded together in the c direction by weak hydrogen bonds (Grim, 1953, p. 48). Halloysite $4H_2O$ (fig. 4) has a structure similar to that of kaolinite except that halloysite has a layer of water between each two basic silicate layers and that its structure has shifts in both the a and b crystallographic directions. Bates et al. (1950, p. 468) present data which indicates that halloysite $4H_2O$ has the morphological form of tubes instead of plates as in the case of kaolinite. Halloysite $2H_2O$ is similar to halloysite $4H_2O$ except that most of the water has been driven from between the layers and the tubes tend to split and unroll or collapse.

The data from figure 5 indicate that the kaolinite clay minerals will adsorb most of their water in the first minute. The poorly crystallized kaolinite took up 92 percent in the first minute and the well crystallized kaolinite 56 percent. Halloysite $4H_2O$ did not take up any more water (54 percent) after two minutes; halloysite $2H_2O$ and the well crystallized kaolinite had very little adsorption after four minutes (95 and 78 percent, respectively); the poorly crystallized kaolinite had considerably more water adsorption than the other kaolinite minerals after the initial sorption (125 percent at 120 minutes).

The halloysite $2H_2O$ took up almost twice as much water as halloysite $4H_2O$, and the poorly crystallized kaolinite took up about 50 percent more water than the well crystallized variety.

The interpretation of the sorption curves (fig. 5) is that much of the initial water sorption is by capillary forces and may be considered as principally pore water. After the initial sorption, the poorly crystallized kaolinite from Union County, Illinois, and the halloysite $2H_2O$ from Eureka, Utah, has a second period of water sorption that takes place much more slowly over a longer period of time.

The probable mechanism for the absorption after the initial sorption is probably the splitting apart of kaolinite aggregates or booklets that are more weakly bonded by either stretched hydrogen bonds or van der Waal's forces.

Montmorillonite Group

Structurally the montmorillonites (figs. 3 and 4) consist basically of two tetrahedral (silica) sheets with an octahedral (alumina) sheet sandwiched between them. The montmorillonite layers are in turn usually separated by water layers. Montmorillonite, unlike kaolinite, always has substitutions of Fe^{++}, Fe^{+++}, and/or Mg^{++} for Al^{+++} in the octahedral sheet and in many cases some Al^{+++} for Si^{++++} in the tetrahedral sheets. The excess charges are neutralized by ions on the surface known as exchangeable cations. The above-mentioned structural conditions are probably responsible for the properties of the montmorillonite clay minerals.

The montmorillonites (fig. 6) show a wide variation in their water-sorption abilities. The sodium montmorillonites from Wyoming and hectorite from California take up several times more water than do the other montmorillonites. In 10,000 minutes the sodium montmorillonite took up about 250 percent more water than hectorite did. Hectorite in 1000 minutes took up about twice as much water as did the Arizona montmorillonite. The Arizona and Tatatila took up approximately the same amount of water before the large decrease in sorption rate at $1\frac{1}{2}$ minutes and 1 minute, respectively. The Arizona montmorillonite proceeded to take up more water than the Tatatila. The Tatatila took up only a small percentage of water after the initial sorption. The nontronite took up the least water (162 percent) and the Mississippi montmorillonite, which has calcium and hydrogen as exchangeable cations, took up approximately 20 percent more water than the nontronite. The order of water sorption at 1000 minutes is Wyoming montmorillonite 756 percent; hectorite 464 percent; Arizona montmorillonite 232 percent; Tatatila montmorillonite 184 percent; Mississippi montmorillonite 180 percent; and nontronite 164 percent.

Fig. 6. – Water-sorption curves for the montmorillonite group of clay minerals.

The interpretation of the data, as shown in figure 6, suggests that water-sorption characteristics are a function of the structure and of the exchangeable cations. The Wyoming and Hector montmorillonites for the most part contain sodium as exchangeable cations, but those from Arizona, Mexico (montmorillonite), and Washington (nontronite) contain calcium as the chief exchangeable cations. The montmorillonite from Mississippi contains calcium and hydrogen as exchangeable cations. The data taken from the curves in figure 6 suggest that calcium montmorillonites rapidly will take up between 15 and 17 layers of water based on the Hend-
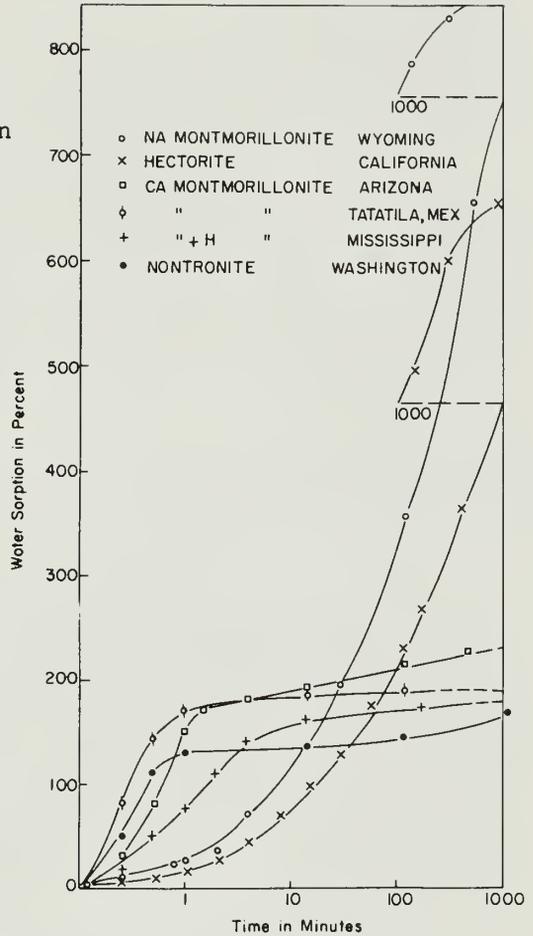
dricks and Jefferson (1938, p. 863-875) configuration. After that, any additional water layers are added more slowly. The Mississippi montmorillonite and nontronite contain larger quantities of iron. If the differences in the specific gravity of the member of the montmorillonite group are considered, the nontronite would probably have about 15 water layers between the crystals instead of 13 as calculated.

The sodium montmorillonites took up more than 50 water layers during the time of the experiment, and the curves suggest that considerably more water would probably have been taken up if the experiment had been continued longer. Graphs from figures 13 and 19 suggest that if Wyoming montmorillonite were allowed to complete its water sorption, it would take up about 140 water layers. Hauser and Reed (1937, p. 913) found that by taking an extremely fine fraction of montmorillonite and treating it with potassium chloride it is possible to obtain a gel with 0.01 to 0.05 percent montmorillonite and 99.95 to 99.99 percent water, which would indicate that the montmorillonite, if all the water is considered to be between the sheets, is able to take up and orient from 2000 to 10,000 layers of water between the two plates of montmorillonite. It is very doubtful that any deposit of montmorillonite in nature will contain so much water, but these figures are given to indicate the tremendous ability that some montmorillonites have for water sorption.

It is easier to understand the mechanism for large uptake of water if the structure of the clay minerals (fig. 4) is considered. If only a layer of water is present, the silica tetrahedral sheets of two adjacent montmorillonite layers may lie close to each other with the cations probably fitting into the holes. The only forces holding these layers together are van der Waal's forces and possibly the exchange cations being attracted by both layers. When water is introduced, the hydration forces of the lattice surface, and also in some cases the hydration of the cations, tend to split the layers apart causing the lattice to expand as revealed by X-ray data (Bradley et al., 1937, p. 217; Norrish, 1954, p. 256). The curves in figure 6 indicate that the initial water sorption for sodium montmorillonites is slower than that for calcium montmorillonites, probably due to the permeability of the montmorillonites.

In the sample of sodium montmorillonite, the particles on the porous disc probably took up a number of oriented water layers before the particles above were able to start adsorption, thus plugging the pore spaces. The first layer was probably adsorbed most rapidly, with diminishing rates for the second and then the third. The second layer of particles probably started to adsorb water after the particles in the first layer made the jump from 22.5A to 40A (Norrish, 1954, p. 256) or the equivalent of six additional water layers that White (1955, p. 199) has attributed to the hydration of the exchangeable sodium ions. The water front probably moves upward as particles above take water from the more weakly adsorbed water layers between the montmorillonite particles below as they in turn add more water layers. This probably continues until the sorption is complete throughout the montmorillonite mass.

The calcium montmorillonite, on the other hand, probably adsorbs one or two more rigid layers of water which do not completely obstruct the pores as they do in the sodium montmorillonite. Therefore, water is transmitted through the mass by capillary action so that most of the particles have access to water almost immediately.

The sodium montmorillonite may have greater total water sorption because the sodium ion and its hydration shell fit more perfectly into the crystalline structure of the oriented water that extends from the surface of the montmorillonite

particles, and thus do not disrupt the orientation of the water net between the particles as much as the calcium ion and its hydration shell may. Robinson and Stokes (1955, p. 121) give the hydration radii of sodium and calcium as 3.3A and 4.2A, respectively. If we assume that the diameter of a water molecule is near 3.0, the sodium ion and its hydration shell should fit into the water network with less interference than the calcium ion and its hydration shell, which is about 25 percent larger.

In addition, the calcium ion with its higher bonding energy may not disassociate as far from the surfaces of the clay mineral as the sodium ion, and, therefore, the calcium ion would tend to reduce the repulsive charge between the montmorillonite flakes. The greater bonding energy of the calcium, the reduction of the repulsive forces between the particles, the van der Waal's forces, and the greater misfit of the calcium ion and its hydration shell would tend greatly to reduce the number of water layers that could be adsorbed when the sodium ion is present.

Mica Group

The mica group of minerals (fig. 4) may be divided into igneous, metamorphic, and clay micas. The igneous and metamorphic micas are divided into species such as muscovite, biotite, and phlogopite. The clay subgroup may be divided into illites and mixed-lattice clay minerals, and these in turn may be classified as trioctahedral and dioctahedral.

The igneous and metamorphic micas contain the highest percentage of potassium, the illites contain an intermediate amount of potassium, and the mixed-lattice clay minerals contain the smallest percentage of potassium. As the crystallite size and potassium content decrease, the water content and the replacement of Al^{+++} by Si^{++++} in the tetrahedral layers increase. There is probably a continuous series from igneous and metamorphic micas through the mixed-lattice clay minerals to montmorillonite that has very little, if any, potassium. None of the potassium in montmorillonite should be fixed as part of the crystal lattice as it is in the micas. All the potassium in montmorillonite should be easily exchangeable, whereas for the micas only part of the potassium is easily exchangeable.

Micas do not expand in water or organics, but montmorillonite, on the other hand, will expand in water and in certain organics. The mixed-lattice clay minerals that have some of the properties of both the true micas and montmorillonite will expand some when placed in water or organic compounds. The amount of expansion will depend on the percentage of potassium in the lattice.

The data from figure 7 indicate that there is quite a variation in the water-sorption properties of the various micas. Muscovite (352 percent) took up about $2\frac{1}{2}$ times more water in 15 seconds than the illite from Grundy County, Illinois, did in two minutes. The Grundy County illite (150 percent) took up almost twice as much water in two minutes as the other micas, except muscovite, did in four minutes. The illite-chlorite (88 percent) from Jackson County, Ohio, took up more water than the Vermilion County illite (72 percent), which in turn adsorbed more than lepidolite (64 percent). Biotite (54 percent) took up the least of any of the micas. After the initial water was taken up (one to four minutes), there appeared to be no more sorption for the micas except for the Grundy County illite, which continued to adsorb water slowly.

Chlorite and Chloritic Clay Minerals

The chlorites and chloritic clay minerals are mica-type minerals which differ from the true micas in having brucite layers that replace the potassium between the mica layers (fig. 4).
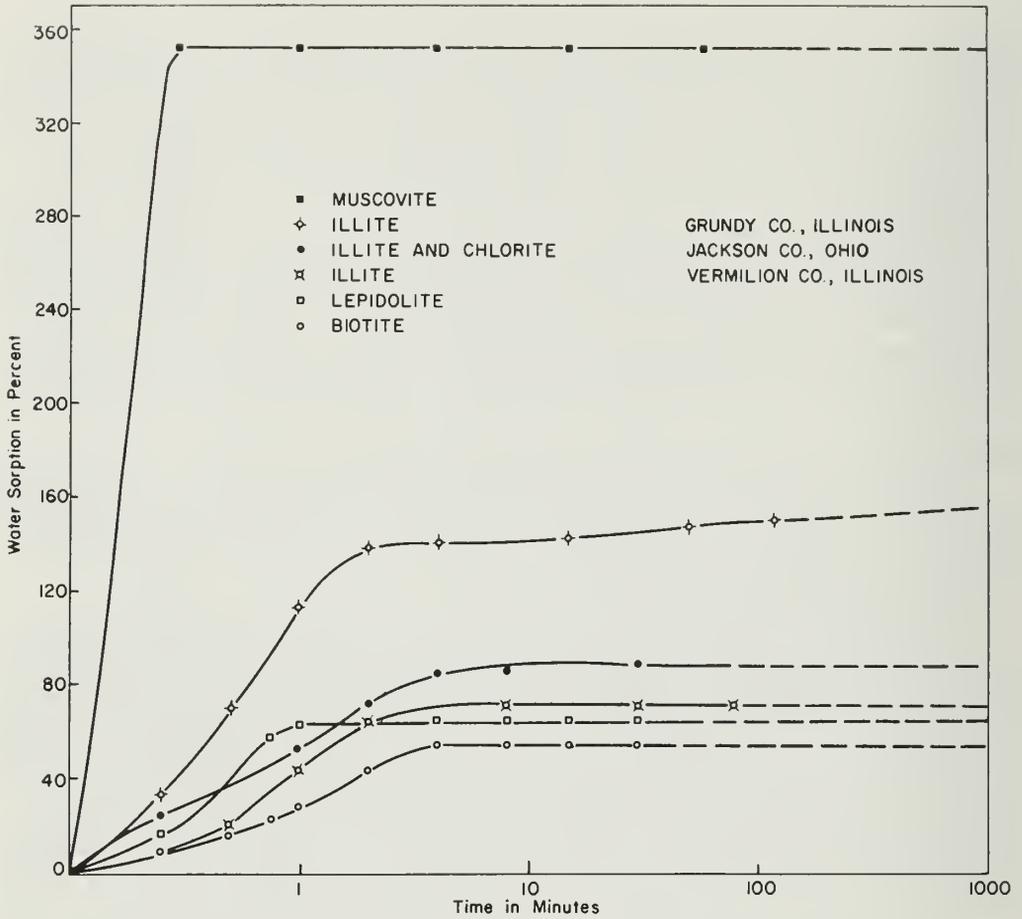
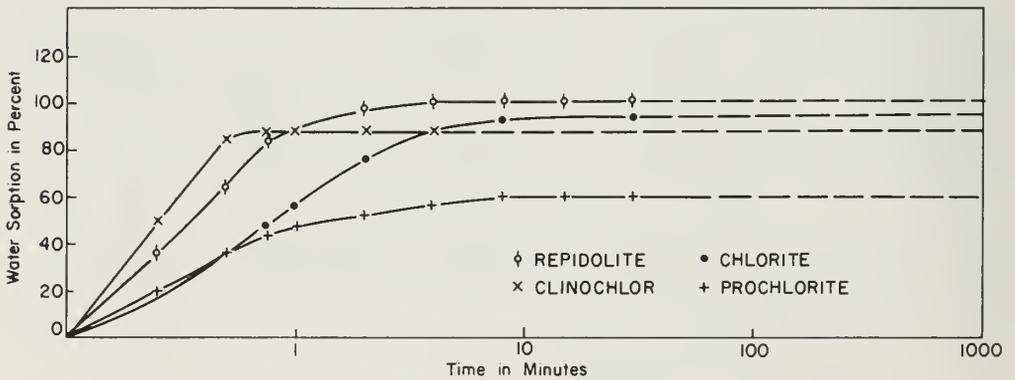Fig. 7. - Water-sorption curves for the mica group of minerals.

Fig. 8. - Water-sorption curves for the chlorite group of minerals.

Chlorites are found in glacial deposits (Beavers et al., 1955, p. 362) and the chlorite clay minerals commonly are found in marine shales and clays (Grim et al., 1957, p. 8; Grim and Johns, 1954, p. 91). At present, no pure sample of the chlorite clay mineral has been found for study, but the curve (fig. 7) of one clay (from Jackson Co., Ohio), which is a mixture of illite and chlorite, suggests that chlorite clay minerals probably have water-sorption properties similar to those of illites.

The chlorites (fig. 8) seemed to adsorb more water than the micas (except muscovite and Grundy County illite), probably averaging about 20 to 40 percent more. After the initial sorption, there appeared to be no more adsorption. The order of water sorption is repidolite (100 percent in four minutes) > chlorite (94 percent in eight minutes) > clinochlor (88 percent in 30 seconds) > prochlorite (60 percent in eight minutes). This could be a function of particle size and packing.

Fig. 9. – Water-sorption curves for the sepiolite-attapulgite-palygorskite clay minerals.

The chlorites give sorption curves (fig. 8) very similar to those of the micas and illites (fig. 7). From the curves it would appear that the same forces are active in the water sorption of both chlorites and micas.

From the structure it would appear that the chlorite clay minerals and chlorites would have about the same physical properties as the illites and micas.

Sepiolite-Attapulgite-Palygorskite Group

Sepiolite, attapulgite, and palygorskite have structures that are similar, as indicated in the generalized structure in figure 4. This type of structure is called a double chain-type structure, similar to that of the amphibole group of minerals. The structures differ from those of the other clay minerals in that the sepiolite-attapulgite-palygorskite structures extend indefinitely in one direction making rod-shaped particles, whereas the structures of the other clay minerals extend indefinitely in two directions making plate-shaped particles. As shown in figure 4, the surface of the rods would be irregular with grooves and ridges on which it might be difficult to orient water for more than a few layers.

The data (fig. 9) indicate that there is a wide variation in the adsorption properties of the sepiolite-attapulgite-palygorskite group. Sepiolite (568 percent) adsorbs the most; palygorskite (460 percent) adsorbs about 100 percent less than sepiolite; and attapulgite (212 percent) adsorbs less than half that of palygorskite. After the initial water sorption, attapulgite behaved like the micas and chlorites by not adsorbing any more water after one minute, whereas sepiolite and palygorskite continued to adsorb water after ten and two minutes, respectively, after the initial water was adsorbed.
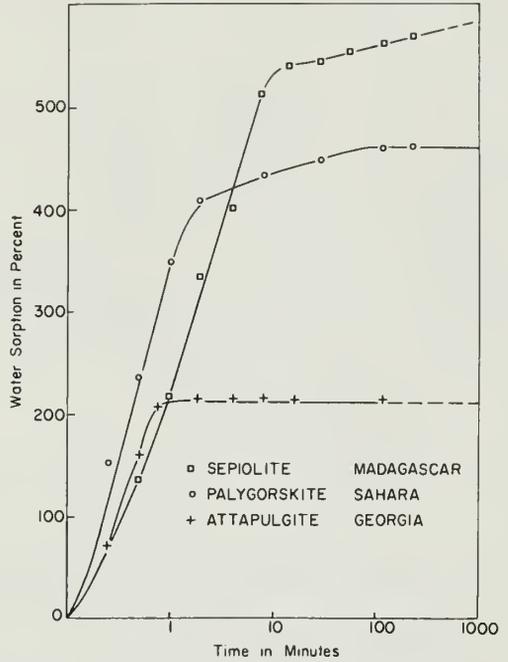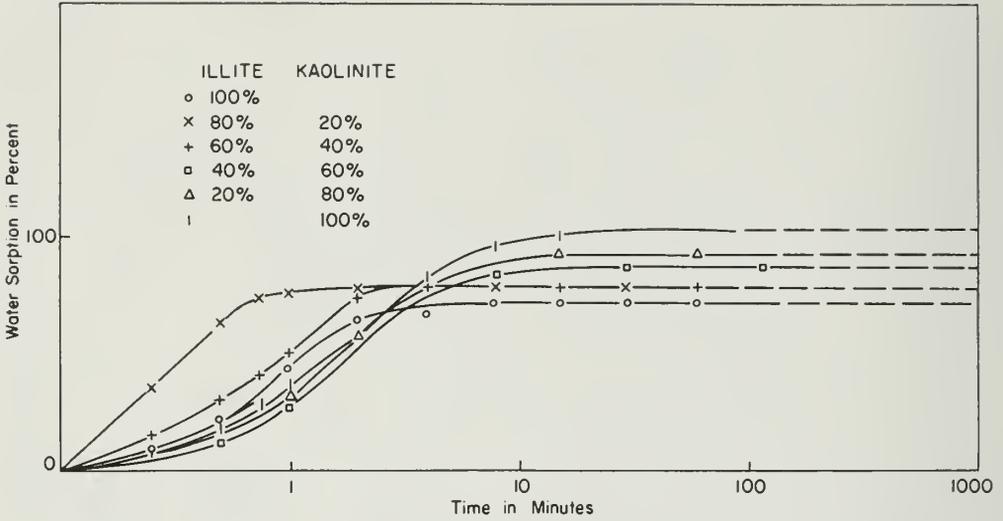
Fig. 10. – Water-sorption curves for mixtures of Union County kaolinite and Vermilion County illite.

The data (fig. 9) suggest that the structure of attapulgite differs from that of sepiolite and palygorskite, or that attapulgite contains calcium as an exchangeable cation and the others contain sodium as the exchangeable cation, or that there is a difference in the particle size. Electron micrographs indicate that attapulgite has narrower fibers than sepiolite (Barbara Collins, personal communication). Nagy and Bradley (1955, p. 885) have suggested a slightly different structure for sepiolite than Bradley (1940, p. 405) proposed for attapulgite. It is suggested that the difference in the properties between the clay minerals may be attributed to differences in crystal morphology which in turn may be due to differences in structure. Since the particles would have a random orientation, the broader particles would tend to create larger pore spaces through which the water could enter, which might explain the higher water sorption of sepiolite and palygorskite.
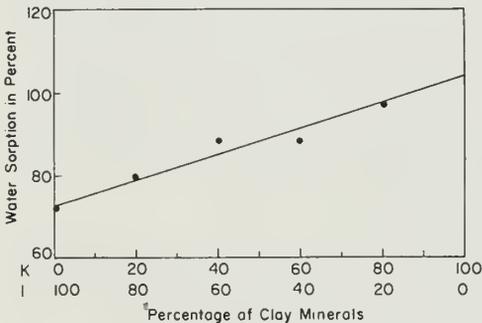
Mixtures of Clay Minerals

The mixtures of minerals used herein are mechanical mixtures of individual clay minerals or clay minerals and quartz.

Kaolinite and Illite

The data (figs. 10 and 11) indicate that the water sorption of a mixture of poorly crystallized kaolinite and illite is proportional to the percentage of each.

Montmorillonite and Kaolinite

In order to determine whether the water sorption of mixtures of montmorillonite and kaolinite is a linear function between the percentages of these clay minerals in the mixtures, the highest

Fig. 11. – Graph showing the linear relation of maximum water sorption for mixtures of Union County kaolinite and Vermilion County illite.

percentages of moisture adsorbed for each mixture was plotted along the ordinate (arithmetic) and the percentages of clay minerals were plotted along the abscissa (arithmetic). The data plotted on figure 13 are obtained from the water-sorption curves of figure 12, which are water-sorption curves for mixtures of Na mont-
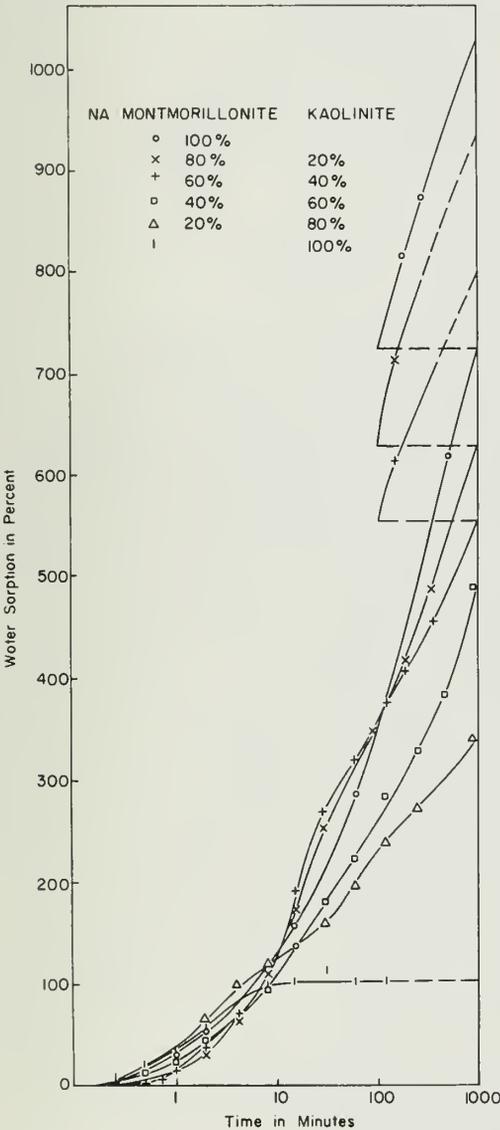

Fig. 13. – Graph showing the linear relation of maximum water sorption for mixtures of Wyoming montmorillonite and Union County kaolinite.
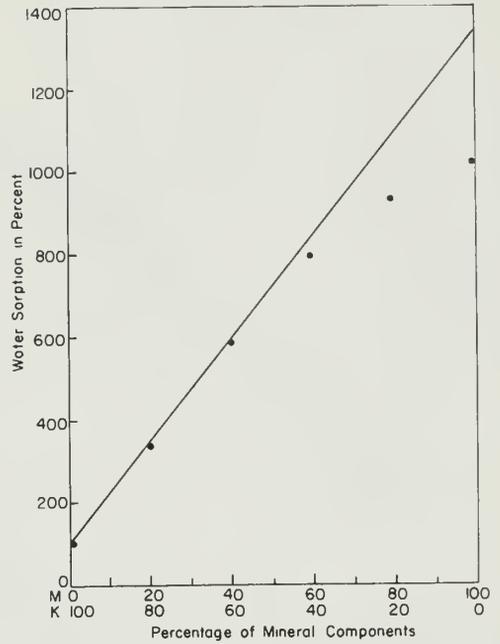
Fig. 12. – Water-sorption curves of mixtures of Wyoming montmorillonite and Union County kaolinite.

morillonite from Wyoming and a poorly crystallized kaolinite from Union County, Illinois. The data on figure 15 are obtained from the curves of figure 14, which are curves for mixtures of Ca+H montmorillonite from Mississippi and the poorly crystallized kaolinite from Union County, Illinois.

In figure 13, if a line is drawn through the points for 100, 80, and 60 percent kaolinite and points for 0, 20, and 40 percent Na montmorillonite, respectively, and if the line is extended to the 0 percent kaolinite and 100 percent montmorillonite line, the result is 1335 percent moisture for the montmorillonite if it is allowed sufficient time to complete its water sorption.

In figure 15, if a line is drawn through the points for 80, 60, and 40 percent kaolinite and points 20, 40, and 60 percent Ca+H montmorillonite, re-
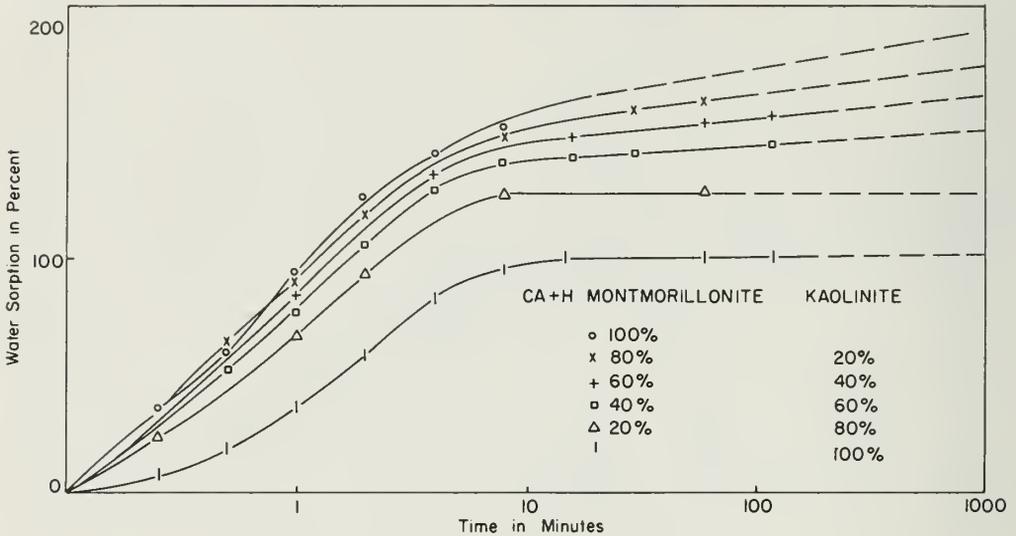
Fig. 14. – Water-sorption curves of mixtures of Mississippi montmorillonite and Union County kaolinite.
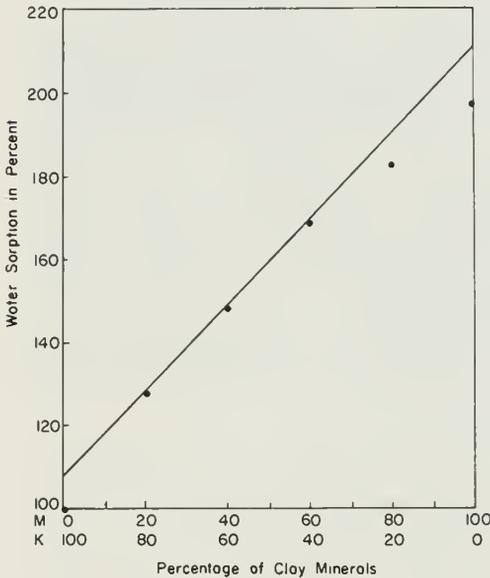

Fig. 15. – Graph showing the linear relationship of the maximum water sorption for mixtures of Mississippi montmorillonite and Union County kaolinite.

spectively, and if the line is extended in both directions, the result is 107 percent moisture for kaolinite and 211 percent moisture for the montmorillonite. The reading of 107 percent for the kaolinite is only about seven percent more moisture than it actually took up. This difference is reasonable inasmuch as the same kaolinite (fig. 5) took up 125 percent moisture when tested at a different time. The difference might be explained by difference in particle size or packing of the material. Since the 20 and 0 percent kaolinite and 80 and 100 percent montmorillonite mixtures were not allowed to complete their water sorptions, it is probably safe to assume that if the montmorillonite had been allowed to complete its sorption, it would have eventually adsorbed 211 percent moisture, which is only 13 percent more moisture than it actually adsorbed.

The data from figures 13 and 15 suggest that montmorillonite and kaolinite mixtures adsorb moisture in proportion to their percentages.
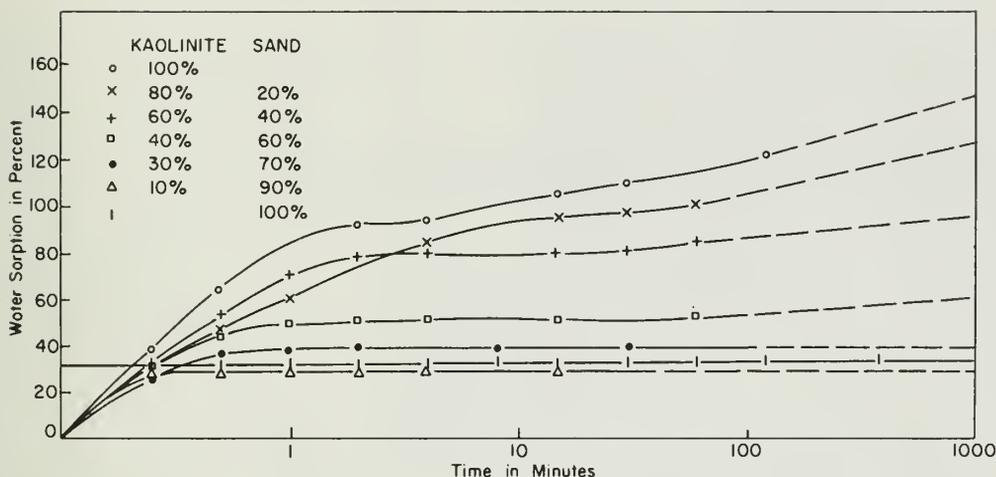
Fig. 16. - Water-sorption curves for mixtures of Union County kaolinite and silica sand.

Kaolinite and Sand

The water-sorption curves of mixtures of poorly crystallized kaolinite from Union County, Illinois, and clay-free silica sand from Ottawa, Illinois (fig. 16), give the data for figure 17. The data from figure 17 suggest that the water sorption for mixtures containing 30 percent or more kaolinite is proportional to the percentage of the kaolinite present. With less than 30 percent kaolinite, the kaolinite sand mixtures do not adsorb water in proportion to the kaolinite present.
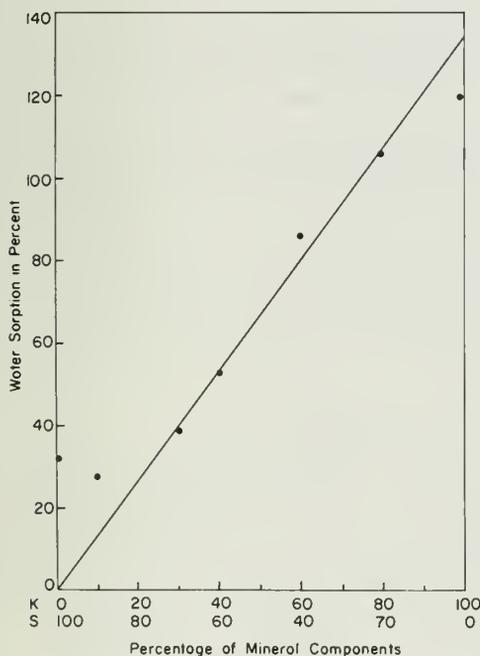
Montmorillonite and Sand

The water-sorption curves of mixtures of Na montmorillonite from Wyoming and clay-free silica sand from Ottawa, Illinois (fig. 18), give the data for figure 19. In figure 19, if a line is drawn through the points for 20, 40, and 60 percent montmorillonite and for 80, 60, and 40 percent sand, respectively, and if it is extended in both directions, the result is about $2\frac{1}{2}$ times greater water sorption for the sand and about 175 percent lower water sorption for 100 percent montmorillonite than is suggested in figure 13. But if a line is drawn through the points for 100 and 80 percent sand and 0 and 20 percent montmorillonite, respectively, and the line is extended to the 100 percent montmorillonite, the result is about 1340 percent water sorption for 100 percent montmorillonite,

Fig. 17. - Graph showing the linear relationship of maximum water sorption for mixtures of Union County kaolinite and silica sand.

which is within 5 percent of that obtained in figure 13. It is assumed that the dashed line on figure 19 is more nearly correct for the water-sorption properties of the montmorillonite-sand mixtures. Another reason for assuming that the dashed line is more nearly correct is that one of the authors (White) in another study allowed the Wyoming montmorillonite to adsorb water for 30 days during which time it took
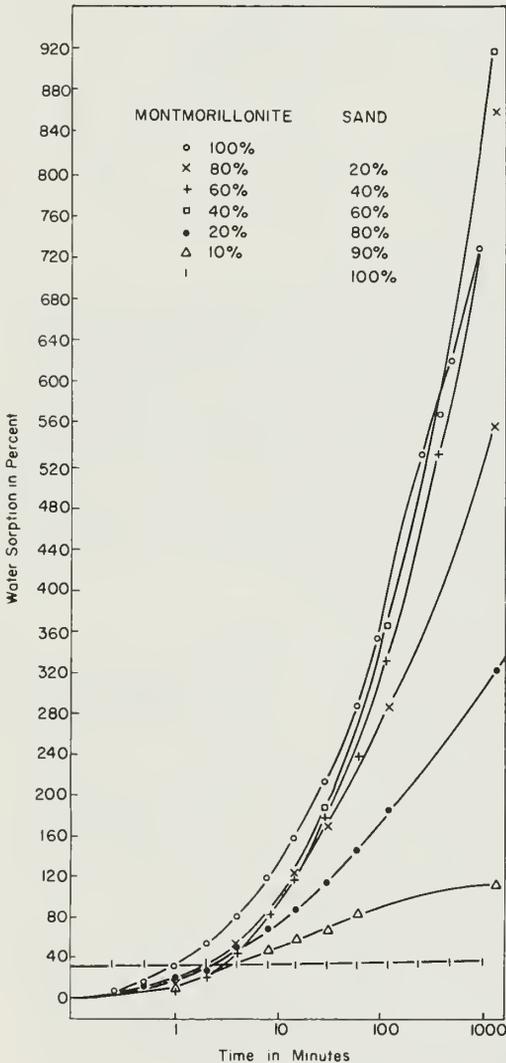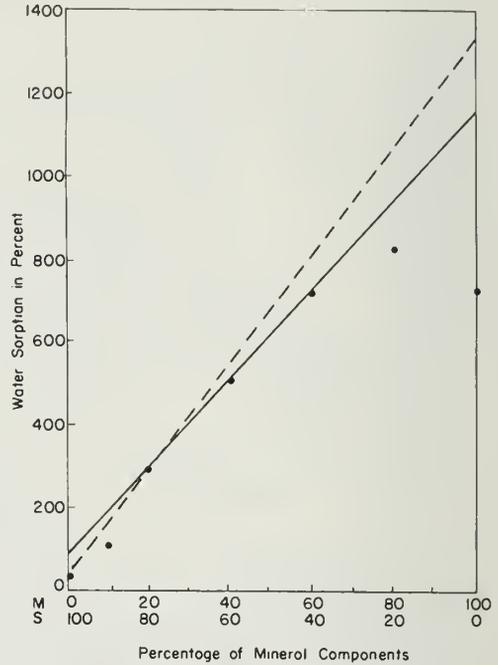

Fig. 19. – Graph showing the linear relationship of maximum water sorption for mixtures of Wyoming montmorillonite and silica sand.

up 1148 percent moisture (after adjustment for evaporation) with no suggestion that the adsorption was near completion.

The data from figure 19 indicate that for less than 20 percent montmorillonite in a montmorillonite-sand mixture, the montmorillonite will not adsorb as much water as the percentage would suggest.

Aggregate Size

The effect of aggregate size was determined on illite, poorly crystallized kaolinite, and Na montmorillonite. The samples for these tests were obtained by crushing and screening air-dried material, and the following grain-size fractions were used: 10-18 mesh, 18-35 mesh, 35-60 mesh, 60-200 mesh, through 200 mesh.

Figures 20, 21, and 22 indicate that the grain size influences the test results.

Fig. 18. – Water-sorption curves of mixtures of Wyoming montmorillonite and silica sand.
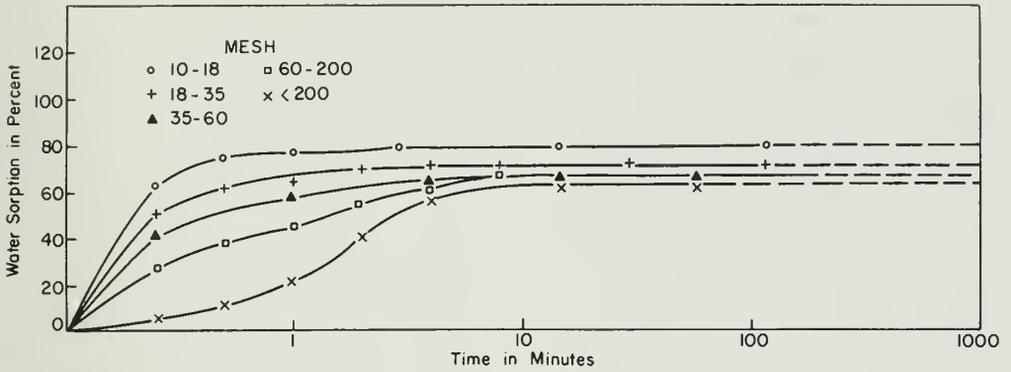
Fig. 20. - Water-sorption curves for Vermilion County illite using various
screen sizes.

Figures 20 and 21 for illite and kaolinite indicate that the coarser the particles,
the more rapidly the water is taken up, and also that the coarser materials adsorb
more water.

Figure 22 for montmorillonite, on the other hand, indicates that for sodium
montmorillonite, the 35- to 60-mesh fraction takes up water more rapidly at first
than the other particle sizes, but after one minute the 18- to 35-mesh fraction be-
gan to adsorb water more rapidly than the 35- to 60-mesh, and the 18- to 35-mesh
from one minute to about 30 minutes adsorbed water more rapidly than any of the
other fractions. After 30 minutes and up to a little more than 1000 minutes, the
10- to 18-mesh fraction adsorbed water more rapidly than the other fractions. The
200-mesh fraction started water sorption more slowly than the other fractions, but
began to gain on the other fractions after 100 minutes. Even after 1000 minutes
the less-than-200-mesh fraction had not adsorbed as much water as the other
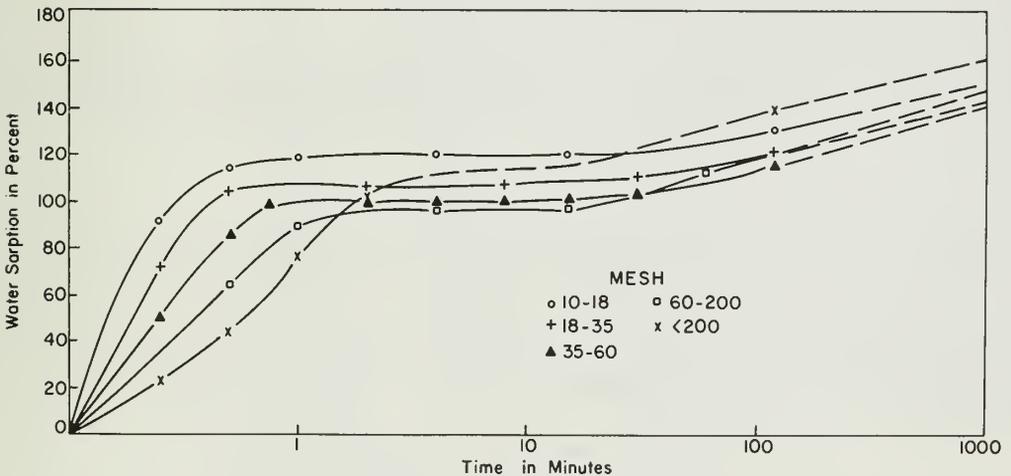fractions.

Fig. 21. - Water-sorption curves for Union County kaolinite using various
screen sizes.

Figure 20 indicates that for the illite the difference in the water sorption is due largely to the amount of void spaces among the fractions, with the 10- to 18-mesh fraction having the most void spaces and the less-than-200-mesh having the smallest amount of void space. In addition to the water entering the void space, some may have penetrated between the illite layers.

Figure 21 suggests that the first water taken up by kaolinite fills the void spaces. The curves (fig. 21) suggest that after 30 minutes some more water is taken up. This later adsorption is probably due to the water's prying some of the more tightly bound crystallites from the aggregates and filling the spaces between.

Figure 22 shows that for sodium montmorillonite there is a rather rapid initial water sorption for all sizes larger than 60 mesh. This is probably because swelling of the aggregates allowed void spaces to remain open as the swelling progressed, and the water could reach all points by capillary action. As the smaller voids swelled shut they became less permeable to water. Further evidence of this was given by tests in which the 35- to 60-mesh fraction took up water most rapidly until the pores swelled shut, the 18-to 35-mesh fraction swelled most rapidly from about 200 to 1050 percent water, and the 10- to 18-mesh fraction swelled most rapidly above 1050 percent moisture. The different water-sorption rates for the different fractions seem to be due to the ease with which the water is able to penetrate the samples through the largest number of capillary channels at any given time.
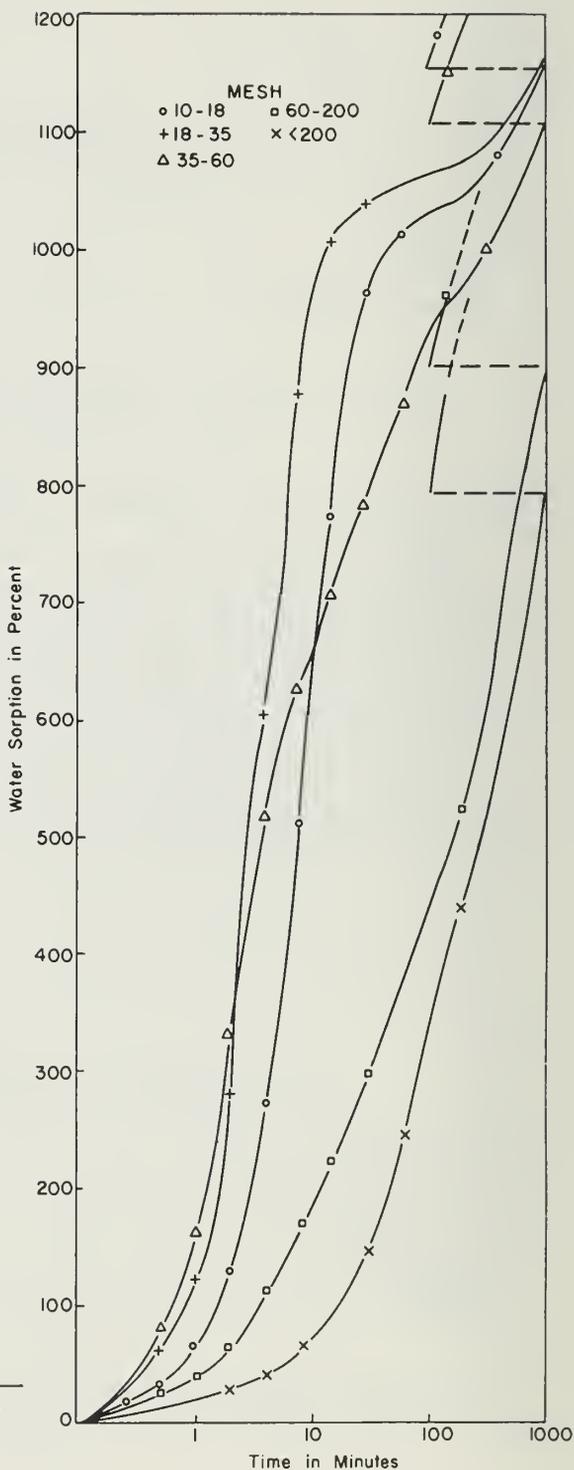

Fig. 22. – Water-sorption curves for Wyoming montmorillonite using various screen sizes.

CONCLUSIONS

1. In kaolinite and halloysite, water sorption takes place rapidly.

2. In montmorillonites the rate and amount of water sorption depends to some extent on the exchangeable cation. The montmorillonite adsorbs water more slowly than the other clay minerals and also adsorbs more water than the others. The sodium montmorillonite will adsorb considerably more water than will the calcium montmorillonites.

3. The water sorption for the micas is completed in a few minutes.

4. The chlorites have water-sorption curves similar to those of the mica clay minerals, biotite and lepidolite.

5. The water sorption for sepiolite, palygorskite, and attapulgite is rapid at first. The water sorption for attapulgite was completed in one minute and was nearly completed for sepiolite and palygorskite in four minutes. Attapulgite differed from the other two in that water sorption was completed after the initial adsorption.

6. Only sodium montmorillonites adsorbed more water than sepiolite and palygorskite. Attapulgite adsorbed about the same percentage of water as did the calcium montmorillonite.

7. Mixtures of clay minerals will adsorb water in the proportion of the clay minerals present.

8. Mixtures of sand and kaolinite will adsorb water in the proportion of the kaolinite in the mixture when kaolinite is in excess of 30 percent.

9. Mixtures of sand and montmorillonite will adsorb water in proportion to the amount of montmorillonite present.

10. For kaolinite and illite, the larger the particle size (up to 10-mesh) the more rapid the water sorption.

11. For montmorillonite, the optimum pore space size for water sorption is evidently the size range of voids that occur in aggregates that pass through an 18-mesh screen and remain on a 35-mesh screen.

ACKNOWLEDGMENTS

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