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U.S. Department of Agriculture
Soil Conservation Service
Engineering Division

Technical Release No. 28
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CLAY MINERALS

by

John N. Holeman, Geologist

PREFACE

The purpose of this technical release is 1) to assemble some of the published information on clay minerals as related not only to geology but also to chemistry, soil mechanics and physics; 2) to condense and coordinate this information for the use of interested SCS personnel; and 3) to present both theories and basic facts concerning clay minerals as well as their applicability to engineering geology. It is realized that some aspects of clay minerals are only mentioned sketchily while other features are covered in considerable detail; however, this is deemed desirable in the first case for the sake of brevity and in the latter to achieve coherence.

The need for assembling data on clay minerals for use within the Soil Conservation Service was first proposed by A. F. Geiger, Geologist, SCS. The preparation of this paper was made at the direction of L. C. Gottschalk, Geologist, Engineering Division, SCS, Washington, D.C. This paper was reviewed and valuable suggestions were made by many interested personnel within the SCS, particularly the staff of the Assistant Administrator for Soil Survey, Dr. C. E. Kellogg; the Head of the Soil Mechanics Laboratory, R. S. Decker, and his staff; the late E. F. Dosch, Geologist, Engineering Division, Washington; the Engineering Geologists in the EandWP Units; and especially E. M. Flaxman and J. L. Hunt, Watershed Geologists.

A primary source of material was "Clay Mineralogy" by Ralph E. Grim (see reference no. 9). Permission from the McGraw-Hill Book Company, Inc. to reproduce parts of this text is appreciated. For those interested in a more detailed study of clay minerals, this textbook is recommended.

Thanks are extended to Professor Paul F. Kerr of Columbia University for allowing the reproductions of electron micrographs and related data.

Many of the terms defined in the glossary are taken from the 1957 Yearbook of Agriculture, SOIL. For additional sources and for further exploration of this subject the texts in the reference list are just a few good examples of the large amount of information published about clay minerals.

The final responsibility for the information included and the manner of presentation rests with the writer:

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CLAY MINERALS

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CLAY MINERALS

Introduction

Since antiquity clay materials have been investigated because of their importance in agriculture, in ceramics, in construction and other uses. It was early recognized that soils containing clay could have the same color, texture and general appearance yet differ widely in other characteristics.

With the development of standard chemical analyses it was determined that the finest clay fractions were composed of silica and one or more of the following: alumina (most common), iron oxide, magnesia, potash and various other oxides. It was also found that two clay materials with the same chemical constituents often had very different physical properties and, on the other hand, that clays with the same physical properties might have dissimilar chemical compositions. It then became apparent that clays varied not only in their chemical content but also in the manner in which they are combined.

Until recently, very little was known about the fundamental nature of most clay materials. With the development of x-ray diffraction analyses, it was found that soil materials are composed of crystalline particles and that a limited number of different crystalline minerals are likely to be found. From this information, the clay mineral concept was developed in the early 1930's. This concept in part states that clays are composed primarily of extremely small crystalline particles of one or more members of a small group of minerals which are now called the clay minerals (Grim, 8). These clay minerals are the chief constituents of nearly all clays and largely determine their properties.

With the general acceptance of the clay mineral concept, there has been an extensive investigation of clay materials and a great quantity of literature has been printed. With the development of the electron microscope, knowledge of the shape, size and other physical characteristics of the tiny particles was extended.

The study of clay mineralogy is being made by workers in many different fields and therefore the clay mineral literature appears in a wide variety of publications: in chemical, physical, mineralogical, soils, ceramic and other journals as well as various textbooks.

Glossary

Absorb - take up, assimilate or incorporate: as to absorb gas in a liquid. To suck up, as a sponge absorbs liquid.

Adsorb - removal of ions or molecules in solution to a solid surface; to accumulate on a surface.

Alkali - a water soluble hydroxide or salt of alkali metals (sodium, potassium).

Alkaline earths - oxide of alkaline earth metals (calcium, magnesium).

Amorphous - without form; applied to minerals without definite crystalline structure.

Angstrom unit - a unit of length, 10^{-8} cm.; 1/10,000 of a micron.

Anion - an ion carrying a negative charge of electricity (caused by a gain of electrons); a negative ion.

Bonds - electrical forces holding atoms together to form molecules.

Cation - an ion carrying a positive charge of electricity due to the loss of one or more electrons. The common soil cations are calcium, magnesium, sodium, potassium, and hydrogen.

Cation Exchange - the exchange of cations held by the soil-adsorbing complex with other cations. Thus if a soil-adsorbing complex is rich in sodium, treatment with calcium sulfate (gypsum) causes some calcium cations to exchange with (replace) some sodium cations.

Cation-Exchange Capacity - a measure of the total amount of exchangeable cations that can be held by the soil. It is expressed in terms of milliequivalents per 100 grams of soil at neutrality (pH 7) or at some other stated pH value. (Formerly called base-exchange capacity.)

Clay size - less than 2 microns in diameter.

Colloid - very fine particles less than 1 micron in diameter (after Rolfe et al, USGS PP 334-G.)

Deflocculate - to separate or to break up soil aggregates into the individual particles; to disperse.

Diocahedral - refers to the octahedral layer of the two and three layer type of clay minerals in which only $2/3$ of the possible internal atom positions are filled with cations (usually by aluminum).

Dipolar - having two poles as a result of separation of electric charge. A dipolar molecule orients in an electric field.

Dry Density - the dry weight or mass per unit of volume. Often expressed as grams per cc. or pounds per cubic foot.

Exchange Capacity - (see cation-exchange capacity.)

Ferric Iron - an oxidized or high valence form of iron (Fe^{+3}) responsible for red, yellow, and brown colors in soils. Fe^{+++}

Ferrous Iron - a reduced or low-valence form of iron (Fe^{+2}), imparting a blue gray appearance to some wet subsoils on long standing.

Flocculate - to aggregate or clump together individual tiny clay particles into small groups or granules. The opposite of deflocculate, or disperse.

Hypogene - an adjective applied to mineral or ore deposits formed within the earth by generally ascending waters.

Ion - an atom or group of atoms that have become charged due to the loss or gain of one or more electrons.

Lattice - the structural framework of a clay mineral which is made up by the orderly arrangement of the various atomic components of the mineral. The mineral is held together by the chemical bonds exerted toward each other by the various ions in the mineral. The structural pattern repeats itself indefinitely and regularly; the atoms are linked according to definite angles and distances.

Micron - a unit of length, .001 mm or one-millionth of a meter. Symbolized by mu, μ .

Molecule - a group of atoms bonded together in a characteristic pattern. The smallest part of a substance that can exist and still retain its composition and characteristic properties.

Polar liquid - liquid composed of polar molecules, as water.

Polar molecules - see chapter on ion-exchange capacity.

Trioctahedral - refers to the octahedral layer of the two- and three-layer clay minerals in which all of the possible internal atom positions are filled with cations (as by magnesium).

Valence - the combining capacity of atoms or groups of atoms. Sodium (Na^+) and potassium (K^+) are monovalent, while calcium (Ca^{++}) is divalent.

Weathering - the physical disintegration or chemical decomposition of rocks.

Classification

In an approach to the study of the clay minerals, the first step might be to define the types and classify them into a system or groupings.

There are three principal groups with which we are concerned and they are distinguished by their structure which controls their behavior. These groups are the montmorillonites, the kaolinites and the illites. All three groups are composed principally of tiny crystals with platy shapes. These crystals in turn are composed of layers of molecules stacked like tablet paper. These tabular crystals, of which all three above mentioned groups are composed, are combinations of either two or three sheets of atoms of two main kinds; one of silicon and oxygen atoms (silica layer) and the other a combination of aluminum with oxygen or hydroxyl atoms (the alumina or aluminum hydroxide layer). These layers are united chemically in either alumina-silica pairs (the kaolinite group), or in silica-alumina-silica trios (the montmorillonite and illite groups). This subject is covered more thoroughly under "Structure, shape, size and density."

The following classification is a simplified version of Table 1 in "Clay Mineralogy." (Grim, 9).

Classification of the Clay Minerals ^{1/}

- I Amorphous
 - Allophane

- II Crystalline
 - A. Two layer type (one silica and one alumina)
 - kaolinite group -
 - kaolinite, nacrite, dickite, halloysite

 - B. Three layer type (two layers of silica and one central layer of alumina)
 - 1. Expanding lattice
 - montmorillonite group
 - montmorillonite, nontronite, saponite, hectorite

 - 2. Non-expanding lattice
 - illite group

 - C. Mixed-layer type
 - chlorite group

 - D. Chain structure type
 - attapulgite, sepiolite, palygorskite

Kaolinite group

The name kaolin is derived from the Chinese words "kao ling" meaning "high hill." Kao ling was the name of the hill in China where clays were obtained centuries ago. Kaolin was defined by Ross and Kerr (25) as the "rock mass which is composed essentially of a clay material that is low in iron and usually white or nearly white in color. The kaolin-forming clays are hydrous aluminum silicates of approximately the composition $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and it is believed that other bases, if present represent impurities or adsorbed materials. Kaolinite is the mineral that characterizes most kaolins."

The kaolin minerals are not all of one mineral species but are collectively called the kaolinite group. This group includes the following four clay minerals: kaolinite, dickite, halloysite, and nacrite.

Kaolinite is the most important member of the group. It occurs in residually weathered material and is a common constituent of soil.

^{1/} Condensed by permission from CLAY MINERALOGY by R. E. Grim. Copyright 1953. McGraw-Hill Book Company, Inc..

Dickite and nacrite result from hydrothermal or pneumatolytic alteration. They are rare in clay materials and virtually of no importance commercially. They differ from kaolinite in the way the silicate units are stacked.

Halloysite is similar to kaolinite but the microscopic crystalline particles are elongate rather than equidimensional in shape. Ross and Kerr (26) have recognized two types of halloysite --- "one that is usually white or light-colored, porous, friable, or almost cottony in texture; and another that is dense, nonporous and porcelainlike." The porous, friable type is more hydrous than the other, having an added $2H_2O$. Sometimes the hydrated form is called halloysite and the less hydrous form is metahalloysite. Others call both forms halloysite with description added concerning hydration.

Montmorillonite group

The name "montmorillonite" was proposed by Damour and Salvétat (5) in 1847 for a clay material found near Montmorillon, France. Montmorillonite is both a group name for all clay minerals with an expanding lattice except vermiculite and a specific mineral name. The four most common clay minerals of the montmorillonite group are: montmorillonite, saponite, hectorite and nontronite.

Saponite is similar to montmorillonite except that Al^{+3} is replaced by Mg^{+2} and some of the silicon is replaced by aluminum. Nontronite is the iron-rich end member of the montmorillonite group. Ferric iron replaces the aluminum. These minerals where iron or magnesium substitute for aluminum usually have an elongate form rather than being equidimensional as montmorillonite tends to be.

Vermiculite is similar to montmorillonite although its lattice expands to a lesser degree. It occurs in very small particles mixed with other clay minerals, often in a mixed layer combination.

Bentonite is a term applied to highly colloidal plastic clay material produced by the alteration of volcanic ash in situ. Bentonite is not a clay mineral but rather a clay material formed from volcanic ash and composed largely of montmorillonite, (Ross and Hendricks, 24).

Illite (hydrous mica) group

The illite group is related to but not identical with the white mica minerals. It contains less potash and more water than the true micas. These minerals have commonly been grouped together under such descriptive terms as hydrous micas. The use of these descriptive terms has been due to the realization that specific names should await a better understanding of the group. Illites appear to be gradational between micas and montmorillonites and have a non-expanding lattice.

Amorphous clay

The name allophane has been applied to amorphous clay-mineral materials regardless of composition. The known samples of amorphous clay material show considerable variation in composition, some times approaching the composition of halloysite, in other cases resembling montmorillonite.

The origin and occurrence

The clay minerals are formed in two principal ways: 1) as alteration products due to hydrothermal action, and 2) by weathering processes.

Hydrothermal alteration

Clay minerals formed beneath the earth's surface are not believed to form from magmatic crystallization but result from the action of hot solutions and gases that originate below and are forced up through the rocks of the earth's crust. Most of the elements of hypogene clay minerals come from the rocks infiltrated. The principal materials altered from rock to clay minerals are alumina, silica, alkali or alkaline earths, and iron. This occurs at temperatures ranging from about 100° to over 450°C, and in acid, neutral or alkaline environments. The largest deposits of hypogene clay minerals are the result of the action of thermal waters.

In many bodies of clay material resulting from hydrothermal action the clay minerals are found in zones surrounding metalliferous deposits or associated with geysers and hot springs. The innermost zone is often sericite (the product of altered white mica and closely similar to illite), grading into a zone of kaolinite and then a zone of montmorillonite and chlorite. Chlorite is most abundant on the outer boundary.

Hydrothermal clay mineral bodies have been found, however, consisting essentially of only one clay mineral. Some of these bodies are as large as 100 feet in diameter. In Cornwall, England there is a kaolinite mass which does not extend to the surface but is overlain by a sill suggesting a hydrothermal origin. On the island of Ponza, about 60 miles west of Naples, Italy there is a large mass of almost pure montmorillonite thought to be altered from an extrusive igneous rock. There is a large body of halloysite of hydrothermal origin at Eureka, Utah.

Occurrences of a single clay mineral are not as common as mixtures of various clay minerals. Often the intermixing is to such a degree that an identification of the component clay minerals is very difficult.

Hydrothermal clay bodies commonly are composed of mixed-layer type clay minerals.

Weathering

Weathering processes under varying environmental conditions lead to a variety of clay minerals. Many factors control this weathering process and no general order of the importance of these factors can be established because they are interdependent and their relative importance may vary from one place to another. The clay minerals produced by weathering are variously dependent on the parent rock, climate, topography, vegetation, and length of time involved.

Parent rock.--The chemical content and texture of the parent rock is the dominant factor in determining the clay mineral produced in the early stages of weathering. As the period of weathering lengthens the importance of the climate, topography and vegetation may counteract this influence (Humbert and Marshall, 13).

The presence or absence of alkalies and alkaline earths in the parent rock is the most significant determinant of which clay mineral will develop in the early stage of weathering. Rocks devoid of alkalies can yield only kaolinites or laterites unless alkalies or alkaline earths are introduced from other sources as by ground water.

Climate.--The climate affects the formation of clay minerals in three ways; by the temperature, the rainfall and the seasonal distribution of rainfall. In warm humid climates the alteration of parent rock proceeds most rapidly. Where the annual rainfall is heavy and well distributed the movement of water through the soil is downward and the soluble components are leached from the weathering zone. In a dry climate or one with long dry seasons the prevailing movement of water may be upward through capillary action and the decay components would not be removed. The climate determines the amount and kind of vegetation and the products yielded by the decay of the organic material.

Topography.--Topography influences the rate of erosion and therefore the rate of fresh parent material exposed to weathering. It also largely determines the direction of vertical movement of water through the weathering zone. If there is high rainfall, low flat areas may become saturated for long periods creating weakly oxidizing or reducing conditions. In these areas movement of water through the soils would be minimal, resulting in little leaching.

Vegetation.--The amount and type of vegetation and the products of its decay help determine the clay mineral produced by weathering. Where vegetation is absent or in areas with long hot dry seasons where vegetal materials are quickly oxidized, little or no organic acids form to act on the weathering zone. Deciduous forests associated with cool humid conditions yield organic products to the soil which have a drastic effect on parent silicate minerals. In another case, a cover of prairie grass in a temperate climate will produce different decomposition products with less active alteration of parent minerals.

Time.-- All rocks can be weathered by the action of normal surface conditions when sufficient time exists for the completion of the process. The minerals produced by weathering may vary with time. In the early stages of the weathering of some rocks, alkalies and alkaline earths may be present in the zone of alteration and, for example, a montmorillonite will form. However, after a long period of weathering all of the alkalies may have been removed by leaching and the clay mineral formed could be a different type in an initial stage of weathering from that of a later stage. "The factor of time is most important when weathering in general is moderately severe and when the parent rock has a composition permitting the formation of a variety of alteration products," (Grim 9).

Environment of alteration

The presence or absence of alkalies and alkaline earths, especially potassium and magnesium, and the amount of time they remain in the environment of alteration are important factors in determining which clay minerals will be produced (Keller 14).

The presence of potassium is conducive to the formation of illite; magnesium to the development of montmorillonite.

Although the knowledge of the mineralogy of clay material is increasing significantly, the occurrence, origin and alteration of the clay minerals still need much more investigation. Kaolinite, montmorillonite and illite all appear to arise from the weathering of many kinds of rocks under various climatic conditions. All are found in residual soils. Certain conditions conducive to the formation of each of the clay mineral groups have been determined. Kaolinite seems to develop in an acid environment from which Ca, Mg and Fe are removed; for example, evaporation. Kaolinite may be expected where leaching is intense and where strong oxidation of inorganic and organic matter prevails. Montmorillonite, on the other hand, requires an alkaline environment in which Mg, ferrous Fe, and Ca are present. Partial or incomplete leaching tends to yield montmorillonite, thorough leaching is conducive to the formation of kaolinite. Illite seems to be formed mainly in a marine environment. It requires the presence of Ca, Mg, ferrous iron and potassium. Chloritic clay minerals require moderate amounts of magnesium, so their formation would proceed more rapidly in the ocean rather than in an environment of leaching (Pettijohn, 21). Where large amounts of magnesium are present, attapulgite-sepiolite may result.

In contrast to the above mentioned influence of saline waters, when clay minerals and clay-size residual debris are transported into a fresh water environment, as a lake or river, there seems to be little change in composition.

Some clay minerals, however, can be weathered or altered through change of environment. The removal of potassium from illite, for example, is possible under certain leaching conditions producing degraded illite or possibly montmorillonite. Kaolinite may be altered to bauxite by the leaching of silica. The changes are reversible, however, and in the proper environment degraded illite may take up potassium; the bauxite may be converted to kaolinite.

Kaolinite is most common in continental and near-shore sediments but is seldom found in marine black shales rich in organic matter. Illite is the predominant clay mineral in all sediments. On an overall basis illite is probably as abundant in clay-size material as quartz is in sand- and silt-size material. Montmorillonite is most common in Tertiary deposits where it was formed by the alteration of volcanic material. However, montmorillonite is also common in Mesozoic and upper Paleozoic sediments.

Charles E. Weaver (33) has concluded that the great majority of clay minerals in sedimentary rocks are detrital in origin and strongly reflect the character of their source material. He finds that X-ray analyses of the clay minerals from thousands of sediments indicate that any of the major clay minerals can occur in abundance in any of the major depositional environments and there is no consistent coincidence between specific clay minerals and specific depositional environments. The basic clay mineral structure is derived from the parent material, and the depositional environment, according to Weaver, has only a secondary influence through modification caused by adsorbed cations. Therefore, it can be seen there is still controversy regarding the importance of the various factors involved in the formation of clay minerals.

Occurrence

Soils may contain in their clay fraction one or several of the different clay minerals but generally one is dominant and contributes its characteristics to the behavior of the soil. The kind of clay mineral may be inherited directly from the parent material, may be developed in the soil, or may be altered from one type to another in the soil environment. No absolute generalizations can be made concerning where one clay mineral or another will be found. However, kaolinite is most common in the red and yellow podzolic soils of the Southeast; illite and vermiculite in the glaciated soils of the Northeast; illite in the gray-brown podzolic soils of the North Central and Lake States; and montmorillonite and illite in the prairie soils of the Cornbelt and the dark-colored soils of the Great Plains. Montmorillonite is found in the Black Belt areas of Alabama and Texas (Cady 3).

Structure, shape, size and density

General

Sands and silts are made up more of quartz than of any other mineral, but the clay size is ordinarily made up of one or more of a rather special group of minerals called the clay minerals. Clay is a general and ambiguous term which means different things to different people. One definition is a natural material with plastic properties; another refers only to size, being a composition of particles smaller than $1/256$ mm or about 4 microns (an upper clay size boundary of 2 microns is being increasingly adopted). A third definition of clay is an essential composition of very fine crystalline fragments of minerals that are primarily hydrous aluminum silicates. The term clay implies nothing regarding origin, but is based on properties, texture and composition which are, of course, interrelated - for example, the plastic properties are a result of the constituent minerals and their smaller grain size.

When referring to texture the term "clay size" is preferred to just "clay"; similarly, in terms of composition "clay mineral" should be used.

Micas are the closest relatives to the clay minerals both in internal structure and form, a platy shape being common more or less to both.

Structure

The clay minerals may be classified on the basis of the present knowledge of their structure and composition (see page 5). The first division is into amorphous and crystalline groups, although the amorphous clay minerals are of minor importance. The crystalline clay minerals are the main constituents of nearly all clay materials and, therefore, the components which largely determine their properties. These crystalline clay minerals are subdivided into four groups according to their atomic structure: those with two layers; three layers; mixed layers; and chain structure. As would be expected, this variation of atomic structure controls the shape of the clay minerals.

One layer is composed of atoms of silicon surrounded by oxygen. These form in a regular pattern making up a tetrahedron. In each tetrahedron a silicon atom is equidistant from 4 oxygen atoms. The chemical relationship of each tetrahedron may be expressed as SiO_4 . These tetrahedrons of silica are linked together to form a hexagonal network of the composition Si_4O_{10} when repeated indefinitely (See figure 1 below). The tops of the tetrahedrons all point in one direction, and the bases are all in one plane.

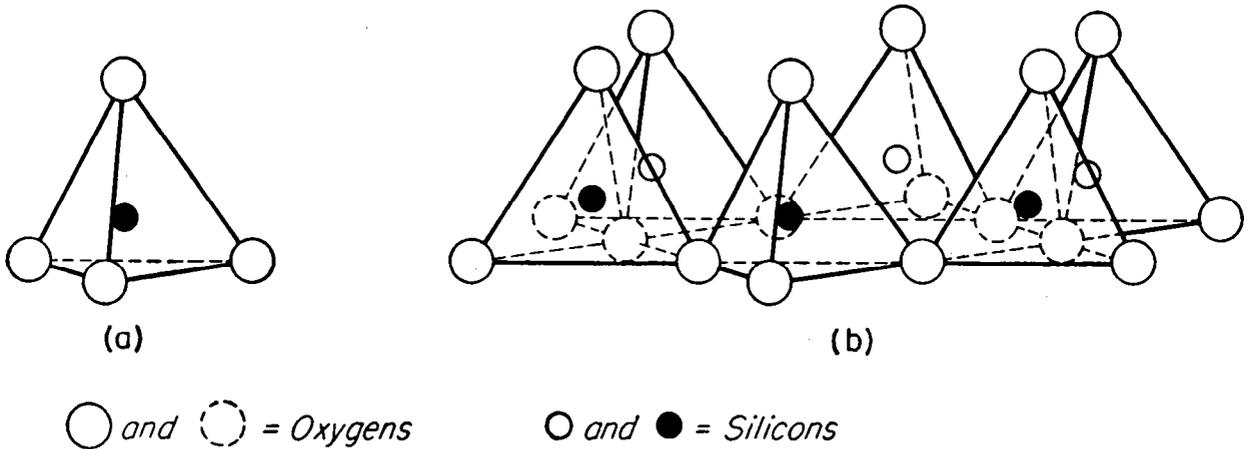


Figure 1. Diagrammatic sketch of (a) single silica tetrahedron and (b) the hexagonal combining form the tetrahedrons assume in the silica layer. From Clay Mineralogy by Grim. Copyright 1953. McGraw-Hill Book Company. Used by permission.

This silica layer may be viewed as a sheet of loosely packed oxygen atoms with each oxygen linked to two silicon atoms directly beneath. It may be recalled silicon has a valence of +4 and oxygen has -2. The silicon atoms are in tetrahedral coordination, three valences being satisfied by linkage to three oxygen atoms in the underlying sheet. The fourth silicon valence is satisfied by an oxygen atom above.

The second layer or structural unit involved in the atomic lattices of most of the clay minerals is the alumina or aluminum hydroxide unit. This layer consists of two sheets of closely packed oxygens or hydroxyls between which aluminum atoms are embedded in such a position that they are equidistant from 6 oxygens or hydroxyls. These 6 oxygens or hydroxyls and one aluminum ion form an octahedron. At times, instead of aluminum, magnesium or iron is embedded in this octahedral coordination and more rarely, chromium, lithium, manganese or other ions may occupy this position.

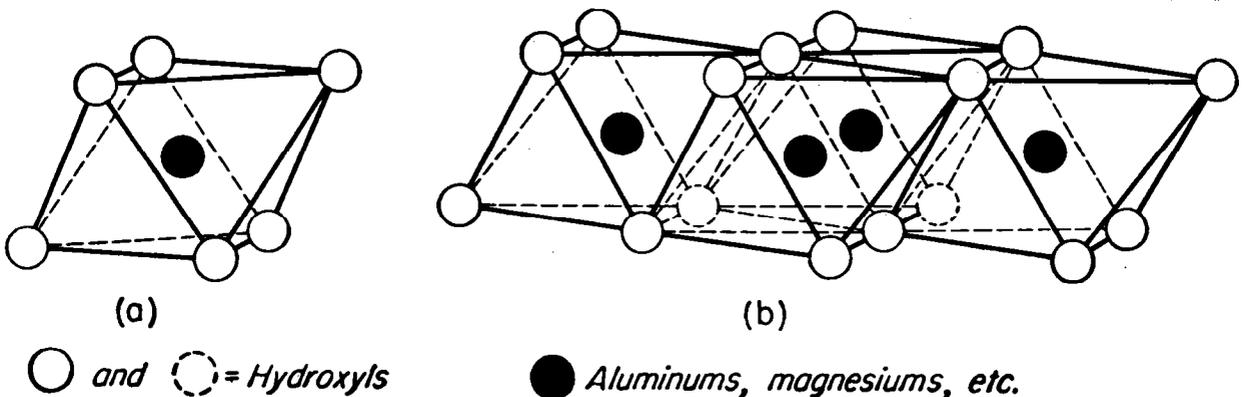


Figure 2. Diagrammatic sketch of (a) a single alumina octahedron and (b) the alumina layer formed by the combined octahedrons. From Clay Mineralogy by Grim. Copyright 1953. McGraw-Hill Book Company. Used by permission.

In the alumina layer only two-thirds of the possible central positions are filled with Al atoms. This is called gibbsite structure, and is $\text{Al}_2(\text{OH})_6$. When magnesium is substituted for aluminum, all positions are filled to balance the structure which is brucite structure, $\text{Mg}_3(\text{OH})_6$, (Grim 10). The valency of Al is +3, Mg +2, and OH -1.

The silica and alumina layers are the primary components of the clay minerals although there may be variations and substitutions in the chemical composition of the layers and therefore, in the physical properties of the clay mineral. Physical properties are determined by the atomic structure.

Two-layer clay minerals.--The kaolinite and halloysite groups are made up of sheets of the two layers, one silica and one alumina. These sheets are stacked in sequence to build up the platy crystal and are firmly bound together. They are immovable and there is no variation in the distance between them. Sometimes these are called the 1-1 clay minerals as well as the two-layer group.

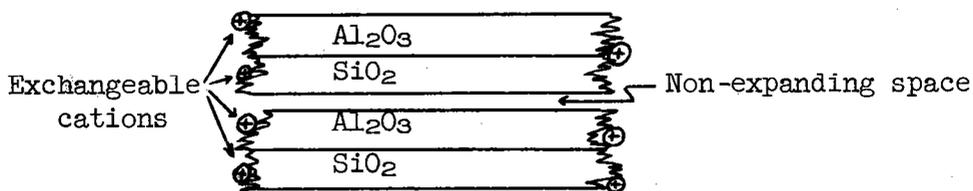


Figure 3. Kaolinite structure ^{2/}

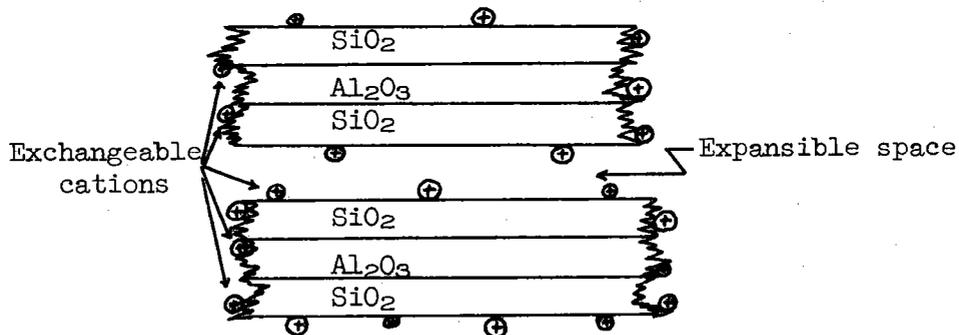


Figure 4. Montmorillonite structure

^{2/} Figures 3, 4, and 6 from "Characteristics and Behavior of Soil Clays" by J. G. Cady (3).

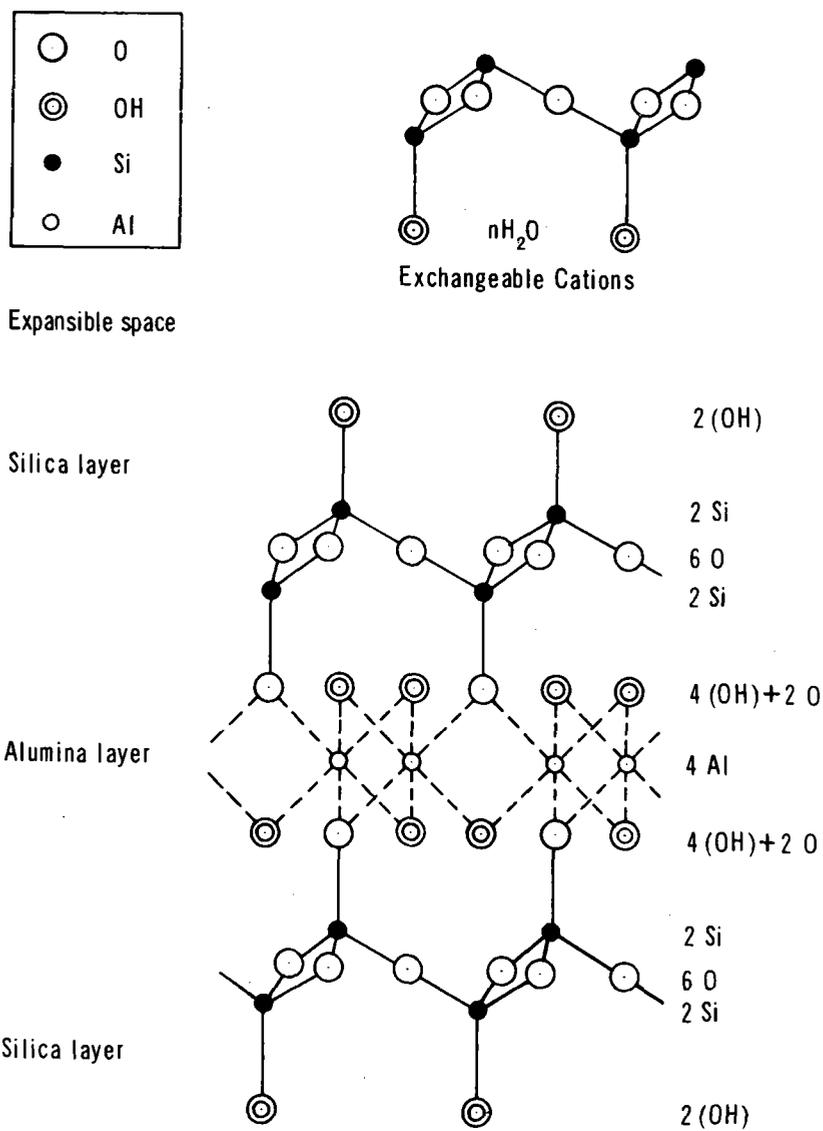


Figure 5. A representation of the lattice structure of montmorillonite - $\text{Al}_2(\text{OH})_4\text{O}_2\text{Si}_4\text{O}_6(\text{OH})_2n\text{H}_2\text{O}$

(After Edelman and Favejee, 6)

Three-layer clay minerals.--The other major group of clay minerals sometimes is called the 2-1 clays because its platy crystals are built up of three layers --- silica-alumina-silica. This group has a number of members which may grade into one another so that sometimes they are difficult to distinguish. However, two main divisions may be made in this group.

The first includes montmorillonite and its close relatives which most strongly express the properties usually thought of as clay-like. (See Figure 4) The montmorillonite group is very sticky and plastic when wet, swells when wetted, shrinks when dried, and has a high capacity to absorb and hold water and other substances. It shows these properties because of its internal crystal structure. In montmorillonites the individual silica-alumina-silica sheets are only weakly bonded to each other. Therefore, these sheets can separate and allow water and chemicals in solution to enter between the sheets. The distance between the bottom of one sheet to the bottom of the next may range from 10 Ångstrom units when completely dry, to 20Å or even 28Å when wet. The ability to expand and contract on wetting and drying, and to open and close the sheets is responsible for some of the "clayey" behavior of montmorillonite. The separation of the sheets increases the net surface area because, of the total surface, about 80% is between the sheets.

A mineral closely related to montmorillonite is vermiculite. It has the property of interlayer expansion, but the sheets cannot separate as far as those of montmorillonite.

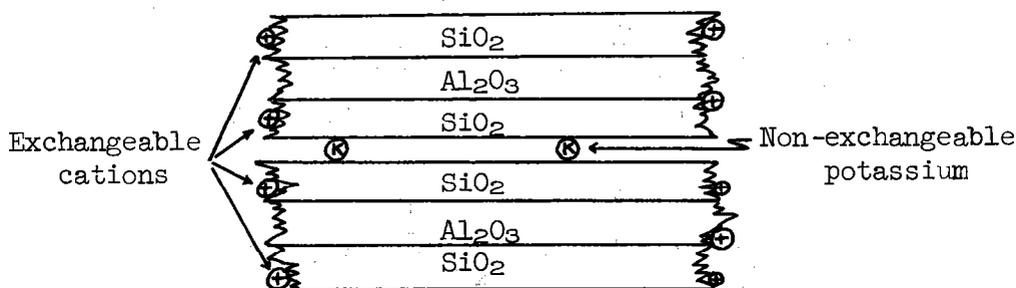


Figure 6. Illite Structure

The other group of 2-1 minerals is called the illite group. Its unit of structure is very similar to that of montmorillonite --- silica-alumina-silica layers forming the sheets, but the sheets are bound together so firmly that they cannot expand. Potassium ions occupy positions between the sheets and bind the adjoining layers of silica together.

Mixed-layer clay minerals.-- A third type of the crystalline clay minerals is composed of mixed layers. The mixed layers may be a regular repetition of different layers resulting in distinctive characteristics. An example of the regular mixed-layer clay mineral is chlorite which might be called a 2-2 mineral. Chlorite is made up of two silica layers alternating with two magnesium or iron layers, or a regular alternation of mica and brucite layers.

The other kind of mixed-layer structure is a random interstratification where there is no regular repetition of layers. There are no distinctive characteristics to such variable combinations of layers; therefore, no specific names can be given to random mixed-layer minerals.

Chain structure clay minerals.-- Some clay minerals are fibrous and composed of different structural units from the three types just discussed, and are the group previously referred to as the chain structures. They resemble hornblende and are composed of silica tetrahedrons arranged in a double chain of composition Si_4O_{11} . This structure is similar to the sheet of silica tetrahedrons in the layer minerals except that it is continuous in only one direction; the other direction is only 11.5 Å wide.

The chains are bound together by atoms of Al and/or Mg in which each atom is surrounded by 6 "active" oxygen atoms. The active oxygens are those with only one link to silicon and hence are those at the edges of the chains and at the tips of the tetrahedrons.

Shape and size

It has long been known that most clay mineral crystals are plate-like and that they readily assume a position in which the flat-face of one platelet tends to rest upon the flat-face of an adjoining platelet. Recent developments in electron microscopy have enabled investigators to obtain more definite information on the configuration of the clay mineral crystals. It has been shown that various clay minerals may exist in extremely thin, flimsy, film-like crystals. Some crystals have been noted with a thickness approximating the unit cell height of 1 millimicron or 10 Ångstrom units. This configuration gives them very high specific surfaces (surface per unit weight) which in turn has a profound effect on the physical properties of these minerals.

The amount of surface in a few grams of finely divided clay can best be appreciated by considering the increase in surface if a one-centimeter cube of massive mica were split into sheets 10 millimicrons in thickness. This operation would increase the surface of the mica cube from 6 sq. cm. to 2,000,000, or an area of about 1/20 of an acre. If these thin sheets of mica should be cut into pieces a few hundred millimicrons in length and width, we would have essentially the size fractions to be found in a fine illitic clay.

The crystals in a few grams of finely divided clay minerals have combined surface areas which therefore can best be expressed in terms of acres. There are no other inorganic substances which have a water holding capacity that approaches that of the clay materials. Six to eight feet of silty clay soils often have sufficient water holding capacity to hold the water equivalent to 40 inches of rainfall.

The clay mineral crystals are extremely flexible, flimsy and fragile. To appreciate this the thinnest clay crystals might be compared to wet sheets of paper with torn edges and with haphazard holes punched in them. The thicker crystals could be likened to cardboard with similar imperfections. When wet with thin films of water or other polar liquids, these crystals tend to orient themselves and stick to other clay mineral surfaces or to other surfaces. Since these crystals are charged, they also attract, orient and organize the molecules of thin films of liquid on their surfaces. These semi-rigid films of liquids serve as lubricants, and become responsible for the high degree of plasticity exhibited by large masses of wet, finely divided and highly charged clay mineral crystals.

If clay mineral crystals are dispersed in water and allowed to flow through a porous medium such as a soil profile, they gradually clog the pores and channels of the soil by adhesion even though these voids are many times larger than the greatest dimension of the clay mineral crystals. The sheet-like nature of these crystals enhances their tendency to form claypans in soil profiles.

The clay minerals occur in most clay materials in particles less than 4 microns (0.004 mm) in diameter. A micron is .001 millimeter. They possess excellent cleavages and when mixed with water, the particles are often reduced in size so that a wet determination of the particle-size distribution will usually show most of the clay minerals less than 2 microns (0.002 mm) even though they are coarser in the crude state.

Vermiculite occurs in macroscopic crystals similar in size to mica. Illite is essentially finely divided mica that has been partially altered by weathering. Large individual particles of clay minerals are found in dickite, a member of the kaolinite group. They measure up to 8 by 8 microns. To illustrate the range in particle size of clay minerals, if a flake of montmorillonite is equated to the size of a standard tablet, (8 x 10-1/2 inches), a flake of dickite might be equivalent roughly to the size of a football field.

In a consideration of sizes and shapes, the old Chinese proverb holds true --- "One picture is worth 10,000 words." Shown below are 5 electron micrographs made by Professor P. F. Kerr (16) of various clay minerals. 2/

3/ Reproduced with permission of American Petroleum Institute and Dr. Kerr.

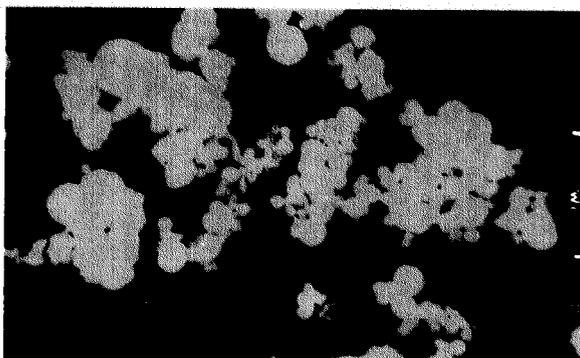


Figure 7. Allophane

Figure 7 is of allophane from Lawrence County, Indiana. As would be expected, allophane, an amorphous material, is found in particles without definite or regular shape. It often shows a rounded, nodular appearance which is perhaps characteristic of that developed by amorphous material on drying.

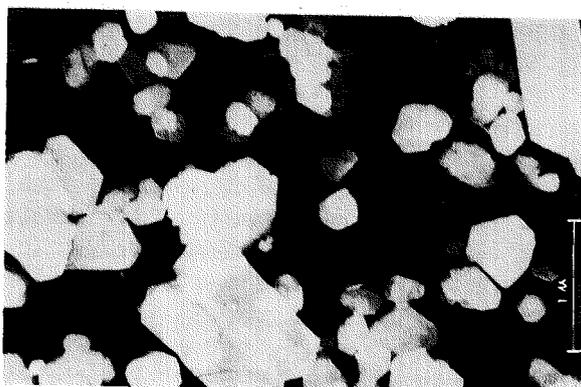


Figure 8. Kaolinite

Electron micrographs of well-crystallized kaolinite show well formed six-sided flakes, often with an elongation in one direction. Figure 8 is a sample of kaolinite from Macon, Georgia. This poorly sorted kaolinite shows well developed crystals, sometimes as elongated and also as overlapping plates. Certain edges of the particles are beveled instead of being at right angles to the flake surface.

Less distinct six-sided flakes are formed in poorly crystallized kaolinite. Often the edges are ragged and irregular.

Electron micrographs of various kaolinite samples have shown particles with maximum dimensions of flake surfaces from .3 to about 4 microns, and thicknesses from .05 to about 2 microns. Larger particles may be present in some clays, but are reduced in size in the preparation of the sample for inspection. This indicates that kaolinite particles are easily reduced to this size but are not reduced to smaller sizes except with difficulty.

Dickite and nacrite have structures similar to kaolinite. Dickite occurs in larger well-formed, six-sided flake-shaped particles, often with a definite elongation in one direction. Dickite particles are often large enough to be studied with the light microscope.



Figure 9. Halloysite

Halloysite, Figure 9, another two-layer mineral, has a morphology unlike that of kaolinite, being elongate and tubular instead of flake-shaped. From some observations, it is apparent that halloysite particles actually consist of rolled sheets, often irregular at the ends. In some electron micrographs the tubular form is indicated by the doughnut shapes seen and believed to be the ends of the tubular particles. The rolled sheets form a tube.

It is not known definitely whether this structure exists in the natural wet clay or results from the drying action.

This electron micrograph of montmorillonite, Figure 10, a three-layer clay mineral from New Mexico, shows an irregular fluffy mass of extremely small particles with no definite crystal outlines. Halloysite is present as an impurity. Usually details of the individual particles are not revealed, but in some cases the larger masses appear to be stackings of flake-shaped units without regular outlines. Some of the particles appear to be about .002 of a micron, or 20 Ångstrom units thick, (one micron being equivalent to 10,000 Ångstrom units). It would seem that at least some of the montmorillonites break down relatively easily into flakes approaching unit cell thickness.

which is about 14 Ångstrom units. Though the shape of the montmorillonite is highly irregular, it has been estimated that the areal dimensions of the flake are probably about 10 to 100 times the thickness.

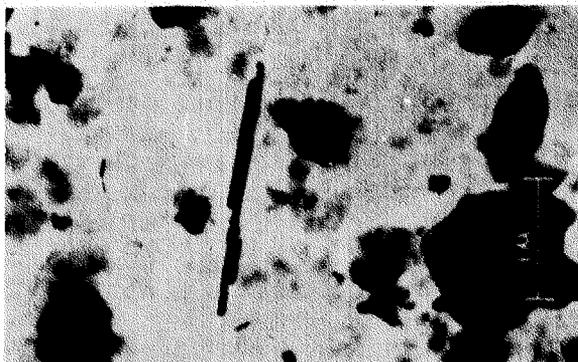


Figure 10. Montmorillonite

Some Mg-rich members of the montmorillonite group, as saponite, seem to be composed of equidimensional flake-shaped units about like those of the aluminum-rich montmorillonites, an exception is hectorite. This fluorine-bearing magnesium-rich montmorillonite is found in thin lathes with a length of about 1 micron and .1 as wide.

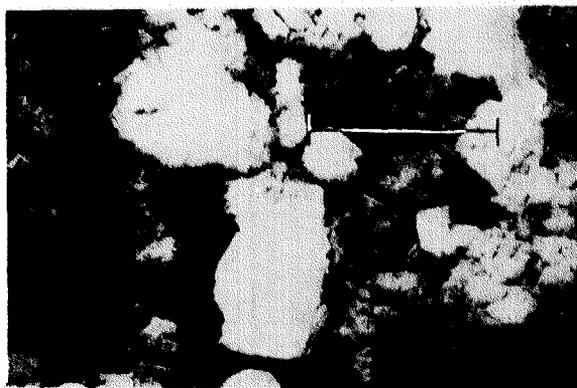


Figure 11. Illite

Figure 11 is illite from Morris, Illinois. It has an irregular flaky structure which is similar to that of montmorillonite except that particles of illite are larger, thicker, and have better defined edges. The essential difference between illite and montmorillonite is that the latter has an expanding lattice while illite is non-expanding since its outside silica layers are bound together by potassium ions.

It is thought that the shape of vermiculite and chlorite would be similar to those of illites except that vermiculite would occur in thinner flakes.

Attapulgite, one of the chain structure minerals, occurs in long narrow fibers. These fibers, or laths, do not appear to have a tubular form as the halloysites do. Their maximum length is about 4 or 5 microns.

Some sepiolites are elongate and fibrous like attapulgite and are called alpha sepiolites. Others consist of extremely small flake-shaped units of irregular outline. These are beta sepiolites.

Density

The density of clay minerals must be measured on aggregates of the minute particles. This measurement is difficult and the results are variable because of inherent characteristics of the clay material. One is that clay material has a relatively high porosity but there is no assurance that the liquid used in the determination will completely penetrate the interstices of the aggregation. Another complicating factor is the possibility of a chemical or physical alteration of the clay mineral during the measurements because of adsorption of the liquid or an exchange reaction between the clay minerals and the liquid used. Clay minerals as they occur in nature contain water and in some of them, such as montmorillonites and halloysite, the water is a basic component of their structure. The density of these clay minerals after dehydration may be determined, but it is not representative of the mineral in its natural state.

In clay minerals such as montmorillonite and illite, which are subject to substitutions within the lattice, the density varies from one specimen to another. For such clay minerals, there is not a characteristic density value, but rather a range of values. (The following density values being in grams per cubic centimeter are also the specific gravity values).

The value for kaolinite is 2.6 grams per cubic cm. This is easily determined because of the low adsorption capacity and general lack of substitution within the lattice of kaolinite.

Halloysite has densities ranging from 2.0 to 2.5 grams per cubic cm.

Illite varies considerably depending on the amount and type of substitution in its atomic lattice, but a value of 2.6 has been considered typical for material with no adsorbed water.

Montmorillonite ranges from about 2.2 to at least 2.7. Probably 2.7 is too low for the iron-rich member (nontronite) of the group.

Chlorite 2.6 to 3.0 grams per cc.

Therefore, it may be seen that the density of the clay minerals ranges from 2.0 gm/cc, the minimum of halloysite, to about 3.0 gm/cc, the maximum density of chlorite.

Ion-exchange capacity

General

The edges of the sheets of all the clay minerals are chemically incomplete, giving the crystal a negative electrical charge. Also, the clay mineral particles have a negative electrical charge due to irregularities and discontinuities in their crystal structure. This negative charge enhances the adsorption of water. Water is made up of polar molecules; that is, the positive charges and negative charges of the atomic constituents are expressed at two different areas of the molecule. The negative electrical charge of the clay mineral crystal attracts the positive area of the water molecule so that molecular layers of water adhere to the crystal and are adsorbed. While the negatively charged surfaces of the particles are involved in adsorption of water they also attract the positively charged atoms (cations) of dissociated minerals which are in solution in the water. Cations of calcium, sodium, magnesium, potassium, and hydrogen have an important influence on soil properties. These ions are exchangeable. One kind of ion in excess in solution can replace another, i.e., take its place on the sheet, pushing the original ion out into solution. The amount of ions held is a measure of the exchange capacity of a clay material or soil. In addition to the charges on the edges of the layers, the 2-1 clay minerals have charges on the faces of the plates including, in montmorillonite, the inner faces of the expanded sheets.

The amount of ions held by a soil is a function of the amount and kind of clay mineral present. Kaolinite, because it does not expand and has exchange positions only at the edges of the crystals, has a very low exchange capacity. Montmorillonite has exchange capacities 10 times that of kaolinite. Illite has intermediate capacities, close to kaolinite.

Definitions and theories

Prior to a discussion involving chemical behavior of the clay minerals a brief review of some of the underlying principles and theories associated with ion exchange may be in order.

1. Polar Molecules.-- Polar molecules have a substantial separation of positive and negative charges, while molecules which are considered non-polar have a relatively small, or no distance between the center of opposing charges. (See figure 12)



Figure 12. Two polar molecules. A is more polar than B.

2. Affinity of ions.-- Electrolytic breakdown of a molecule into atoms furnishes cations and anions (having a net charge of + and -, respectively) with an affinity for one another as well as for the atoms of the solvent in which they are associated.

In any aqueous solution, cations and anions are attracted by water molecules (polar) and the ions become attached to the molecules. The negative ends of the polar water molecules attract the cations; anions are attracted by the positive ends of the molecules.

In the case of the water, the H^+ ions have a greater affinity for the O^{2-} ions than for other ions present. However, after these ions combine, the resulting polar water molecule has affinity for either cations or anions and frequently separates them.

The relationship is not a static condition, but is in a state of constant change. As a result, there is at all times, an abundance of relatively free H^+ and OH^- ions.

Ionization occurs in substances in aqueous solutions and therefore permits exchange reactions which are discussed later.

3. Hydrogen-ion concentration.-- The freeing of H^+ and OH^- ions, as related above, provides a condition by which comparison of the acidity or alkalinity of solutions can be made. The negative logarithm of the hydrogen-ion concentration of solutions is expressed as a pH number. For example, pH 7 indicates an H^+ concentration of 10^{-7} moles/liter and is regarded as neutral. pH values from 0 to 7 indicate decreasing acidity and from 7 to 14 indicate increasing alkalinity and can be used to predict behavior trends and patterns.

The following list indicates the common valence of the chief replacement ions: (Also see figure 13).

Silicon	Si^{+4}	Calcium	Ca^{+2}
Oxygen	O^{-2}	Potassium	K^+
Aluminum	Al^{+3}	Hydrogen	H^+
Magnesium	Mg^{+2}	Iron	$Fe^{+2}; Fe^{+3}$
Sodium	Na^+	Hydroxyl	OH^-

Cation-exchange capacity

Many factors influence cation-exchange capacity and no group of clay minerals has a single capacity value. A range of capacities applies to each group.

A single cation may be sorbed by a clay mineral with a wide range of bonding energies, and this depends on the location on or in the silica-alumina particle where the cation is sorbed; e.g., whether it is held between the sheets of the layered minerals or around their edges. This is an important cause of the variation in exchange capacity. As the lattice structure of the different clay minerals varies, there are different possible positions for the cations and as a result the bonding energy for a cation could be expected to

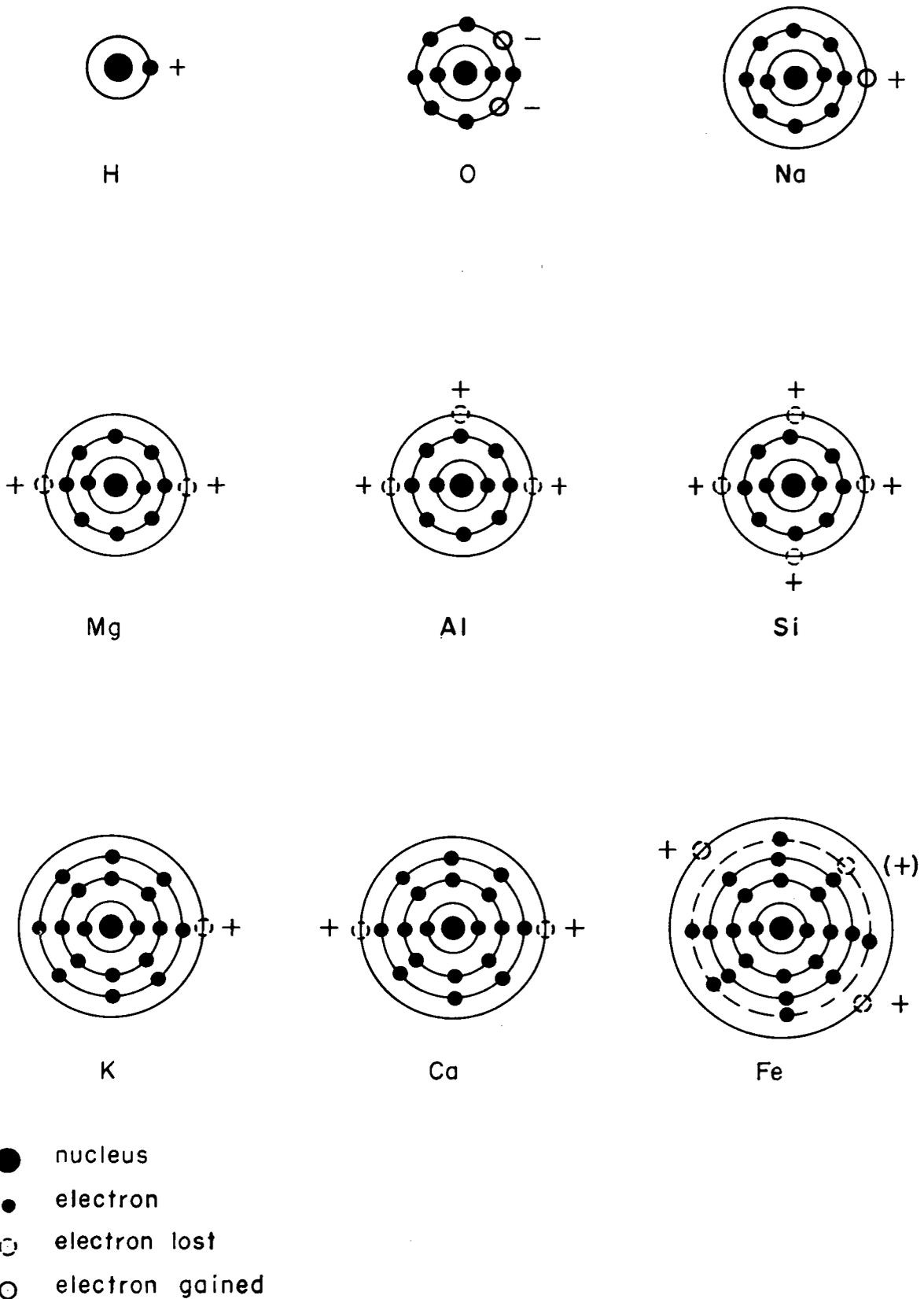


Figure 13. A representation of the structure of some common ions

vary in the separate types of clay minerals. The exchange capacity varies according to the nature of the cation also. For example, in montmorillonite, the exchange capacity is greater for Ca^{++} than for Na^+ . Variations may be caused by other factors such as particle size, lattice distortion, closing of exchange positions, and the pH of the environment.

All inorganic minerals composed of particles with a diameter of 2 microns or less have a small cation-exchange capacity as a result of broken bonds around their edges. As the particle size decreases, this capacity increases, but even in the small size in which non-clay minerals occur, the exchange capacity is generally insignificant. Some organic materials have cation-exchange capacity, but these are found almost exclusively in Recent sediments and soils.

The cation-exchange capacity is usually measured in the milliequivalents per 100 grams, and at neutrality; i.e., pH 7. The range of cation-exchange capacity is: for kaolinite 3-15, illite 10-40, and montmorillonite 80-150 meq. per 100 g.

Mechanics of cation-exchange capacity.-- The cation-exchange capacity of clay minerals is the result of three conditions:

1. Substitution of ions within the clay lattice.-- At times aluminum takes the place of silicon and magnesium substitutes for aluminum causing unbalanced charges in the structural sheets of some clay minerals. These cations, available for exchange because of their lattice substitution, are found mostly on the cleavage surfaces of the layer clay minerals. Occasionally, cations held by forces caused from substitution of aluminum for silicon are virtually non-exchangeable, as the potassium in the micas. The substitutions affecting cation-exchange capacity in the clay minerals are thought to be mainly in the octahedral layer. Perhaps 80 percent of the exchange capacity of montmorillonite and vermiculite is due to substitutions within the lattice structure.
 2. Broken bonds.-- Along the edges of both the silica and alumina layers, broken bonds create negative charges which are balanced by adsorbed cations. The broken bonds occur on the non-cleavage surface; in other words, on the vertical planes of the two-, three-, and mixed-layer clay minerals and the horizontal planes of the chain structure type.
- The number of broken bonds per unit of volume and thus the exchange capacity caused by them would increase as the particle size decreased. Broken bonds are the primary cause of cation-exchange capacity in the two-layer minerals. They are an important cause of ion exchange in illite, chlorite and the chain-structure type clay minerals. However, in montmorillonite and vermiculite they cause a small part of exchange capacity.
3. The replacement of hydrogen ions of the exposed hydroxyls.-- The clay minerals have hydroxyl groups exposed around the broken edges and the hydrogens of these exposed hydroxyls may be replaced by cations which would be exchangeable. This effect on exchange capacity would be important for kaolinite and halloysite as they contain a sheet of exposed hydroxyls on the basal side of the alumina layer.

Environment of the exchange reaction.-- Normally water is present and affords the medium for exchange of cations. Dissociation of ions usually occurs in water solutions. However, clay minerals can take ions from very insoluble matter suspended in water and it is believed that reactions also occur where very little water is present in the environment. Kelley (15) and others have reported that the replacement of ions in clay minerals by ions in solution increased as the concentration of the solution was increased, but not in direct proportion to the concentration.

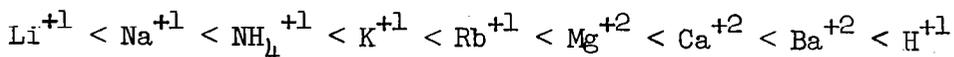
It has been demonstrated that ion exchange can occur between clays and plant roots without the intermediate solution of the ions. It is postulated that exchangeable ions are in a continuous state of thermal agitation, and that where there are adjoining zones of agitation, it is possible for a cation to jump from one spot to another if at the same time an ion of like charge is jumping in the opposite direction thus simultaneously exchanging positions. This direct exchange may take place between clay minerals and other inorganic materials as well as with plant roots. This principle is employed in the application of dry gaseous ammonia as a fertilizer.

Reduction of exchange capacity.-- The presence of Fe_2O_3 may reduce the cation-exchange capacity of clay minerals by neutralization with the positively charged iron oxide particles.

Organic ions and molecules, being large and flat, may blanket several exchange positions and thereby reduce the number. Sulphur compounds may develop on the surfaces of the clay minerals causing a reduction of capacity also.

Nature of the ion

The replaceability of a given ion varies with the nature of the ion. As a rule, the higher the valence of an ion, the greater is its ability to replace another ion or to retain its position if already present on the clay mineral. Hydrogen is an exception as it usually acts as a divalent or trivalent ion. The order of firmness with which exchangeable ions generally are held is represented by the following series (Millar, et al. 20) indicating increasingly strong adsorption to the right:



In other words the calcium will tend to replace magnesium, et cetera. The order of replacement varies somewhat according to the clay mineral, the concentration of solution and other factors. The exchangeable ions most commonly found in clay soils of temperate regions are calcium, magnesium, hydrogen, potassium, and sodium. The first three are dominant except in alkaline or saline soils.

In ions of the same valence, the power to replace tends to increase as the size of the ion increases because the large ions are held more firmly than the smaller ones. An exception to this is the potassium ion which is about the same size as the opening in the oxygen layer of the layered clay minerals and thus becomes "fixed"; i.e., relatively difficult to replace as in illite.

Importance of ion exchange

The property of ion exchange is fundamental and of practical importance in all the fields concerned with clay materials.

In the field of agriculture, nourishment for plants is partly retained in the soil as exchangeable ions and is available for plant growth through exchange reactions. The potash added to soil in fertilizer is retained and made available through exchange reactions between the potassium and clay minerals. Another example is the effect certain exchangeable ions have on the tilth of soil. In soils saturated with calcium ions clay particles tend to aggregate giving a granular texture which increases the porosity and permeability and therefore contributing to good tilth. Soils with an abundance of sodium ions tend to be dispersed and relatively impermeable, thus have unfavorable tilth and low infiltration capacities.

Application of ion exchange

In the construction field, the engineer at times can alter the properties of a soil through exchange reactions to make it more suitable for his purposes. Perhaps the most dramatic alterations have been on the properties of montmorillonitic clay materials. One such property alteration through cation exchange has been on permeability. By changing the calcium variety of montmorillonite to the sodium variety a large decrease in permeability can be induced. This has been accomplished with the treatment of salt water. On Treasure Island in San Francisco Bay the lining of a man-made lake was made more impermeable by such an application of ion exchange. For information on this specific case consult the report by Lee (18). At other times the engineer may unintentionally cause an ion-exchange reaction through raising or lowering the water table or by the installation of concrete which alters the properties of the soil. If the resulting changes in compaction, shrinkage and plastic characteristics are not anticipated the effects could be highly unfavorable.

The clay-water system

General

The principal difference in behavior between a sand and a clay material is due to the special properties of the clay-water system. In order to understand the properties of a clay material, one must understand the liquid phase of the system. Although the liquid portion of the clay-water system does not consist of chemically pure water, it is the water rather than the dissolved ions that has the dominating influence.

The nature of the water

Clay materials contain water in several different states. (All of these states of water are necessary to make up the natural clay-water system.) One classification of these types of water is:

1. pore water.--this is water that fills the voids and may be removed by moderate compressive forces.

2. water that cannot be removed by stresses normally applied but can be removed by drying in atmosphere of low humidity and heating to 110°C . Water of types 1) and 2) represent more or less normal liquid water.

3. water that cannot be driven off by heating to 110°C . This water is either firmly bonded to the clay mineral and adsorbed as a solid (icelike water) or else is a part of the silicate lattice structure as H_3O^+ and OH^- ions (Rosenqvist, 23).

The non-liquid water is the water initially adsorbed by a dry clay and is thought to be in a crystalline state. It accounts for the high cohesive strength of clay minerals. Addition of water in excess of the amount that can be held in the solid state reduces the cohesion of the discrete clay particles and provides a lubricant between the particles thus developing plasticity.

The effect of water on clay properties

The mineralogical composition, particle size, density, geologic age and genesis of clay minerals may vary considerably, but there are some characteristics shared by them all which distinguish clay minerals from other soil components. Plasticity is perhaps the most obvious characteristic of clay minerals. Most of the other properties seem to be closely linked with the condition creating plasticity.

V. M. Goldschmidt found that typical clay properties, especially plasticity, depend on interactions between polar water molecules and the minute plate-like clay mineral particles. If clay minerals are mixed with a non-polar liquid as carbon tetrachloride plasticity does not develop as with polar liquids. These discoveries help us to understand the clay-water system and indicate that a portion of the water in clay-water systems should be considered a part of the clay minerals rather than free pore fluid.

Heat of wetting

When a dry clay is immersed in water heat evolves and this is called heat of wetting. It is considered that this phenomenon is due to 1) a change in the state of water next to the adsorbing surface of the clay mineral, and 2) the possible hydration of the adsorbed ions. The orientation of water molecules in the adsorbed water is thought to be a cause of heat of wetting. The heat of wetting is measured in calories per gram of dried clay which was dried at temperatures below 110°C . There seems to be a relationship between heat of wetting and cation-exchange capacity for natural clay materials. Heat of wetting values for some clay minerals are approximately as follows:

Kaolinite -----	2 calories per gram
Illite -----	4 calories per gram
Montmorillonite - -	12 calories per gram

The effect of time on clay-water systems

When samples of clay materials are remolded with water and are allowed to stand under certain conditions, there may be an increase in compressive strength without a change of water content. The development of

this "air-set" strength in time is caused by the length of time required for water to penetrate to some of the surfaces of the clay mineral particles and for the orientation of the water molecules to take place. This compressive strength is dependent on the formation of the solid water.

In construction work, the effect of this time factor can cause variation between the laboratory findings on strength and sensitivity and the actual field conditions because of the difficulty of duplicating field conditions and evaluating the time factor. Geologists and engineers attempt to avoid this discrepancy by sending undisturbed samples with retained natural moisture content to the laboratory for testing.

Properties of clays as related to engineering uses

General

The term "engineering properties" of a material refers to those properties of the material that have a significant influence on its performance during and after construction operations (Terzaghi, 30). Sediments found in nature consist of particles with different size, shape, and mineralogical composition. If a sample of a sediment is separated by mechanical analysis into various grain-size fractions, the minerals found in each major fraction are often distinctive. The sand- and silt-size fractions are dominated by fresh or slightly altered fragments of rock-forming minerals such as quartz, feldspar, calcite and mica. These are products of physical weathering or disintegration. Equidimensional grains are common in sand and silt, platy grains are typical of the clay size. The percent of equidimensional particles decreases and of platy particles increases with decreasing grain size. The clay-size fraction is dominated by clay minerals such as kaolinite, illite and montmorillonite produced primarily by the chemical weathering of rock-forming minerals.

Physical properties of clay materials that may be important to recognize for the design and construction of earth dams and other functions in SCS programs are porosity, permeability, plasticity, compressibility, shear strength, sensitivity, expansibility and dispersibility. It should be kept in mind that variations in the water table, and thus the moisture content of the sediment, may have a strong influence on these listed properties. These properties can be roughly estimated in the field, but require laboratory tests for precise evaluation.

Porosity

Porosity is the percentage of pore space or voids in the total volume of material. A sediment may be porous without being permeable, but it cannot be permeable without having interconnected pores. For example, a silty clay from Flathead Valley, Montana was found to have a porosity of 55% and coefficient of permeability, K, of only 0.2 gallons per day while a Pleistocene gravelly sand from Nebraska with a porosity of 35% had a K of 8,350 gallons per day (Wenzel 34).

As the grain size of a uniform sediment decreases the porosity tends to increase. Of course, a well-graded sediment will have less porosity than a sediment of uniform size because the smaller particles tend to fill the spaces between the larger particles. For example, a glacial till, GC, may have a

porosity of 20% while at the other end of the range a soft, saturated bentonite, CH, may have a porosity of 84% (Terzaghi and Peck 29).

Permeability

The permeability of a material is its capacity to transmit fluids under pressure. It may vary in different directions. A material is considered permeable if it has interconnected void spaces. The rate at which a fluid flows through these interparticle voids is dependent on the void size and connections, the head and the viscosity of the fluid. The larger the size of the pores and their interconnections the greater the flow of water. It may be seen that coarse-grained soils, having a good distribution of particle size from large to very fine, is relatively impervious because the finer grains fill the space between the larger particles. In clay soils the numerous pores and interconnections are so very small that water movement is severely restricted and the permeability may be negligible in spite of a high porosity.

In clay materials permeability is also influenced to a large extent by the exchangeable ions present. If, for example, the Ca (calcium) ions in a montmorillonite are replaced by Na (sodium) ions, the permeability becomes many times less than its original value. The replacement with sodium ions reduces the permeability in several ways. For one thing the sodium causes dispersion (disaggregation) reducing the effective particle size of the clay minerals. Another condition reducing permeability is the greater thickness of water adsorbed on the sodium-saturated montmorillonite surfaces which diminishes the effective pore diameter and retards the movement of fluid water.

The coefficient of permeability, K , of a given material may be expressed in Meinzer units, which is the rate of flow of water in gallons per day, through a cross-sectional area of 1 square foot, under a hydraulic gradient of 100 percent (1 foot per foot) and at 60°F.

In many permeability tests performed in the laboratory as well as through pumping tests in the field, the value obtained is not in Meinzer units, but is in terms of feet per day, cm/sec., ft/yr., etc. (Cm/sec. may be converted to ft/yr. by multiplying by 10^6). Although these terms are often used as if they were measurements of velocity they are actually volumetric, as are Meinzer units. The definition of feet per day is the same as the above definition of Meinzer units except that cubic feet are substituted for gallons. The k value of a clean, fine dune sand is on the order of magnitude of 2.8 feet per day; that of silt, .028 feet per day; and of clay, .000028 feet per day with a wide scattering from the average. The Corps of Engineers lists the range of permeability of CL and CH as: from 10^{-6} to 10^{-8} cm per second. This very low permeability of a clay makes it difficult to compact when wet and very difficult to drain by ordinary means.

Plasticity

This is the property of a material that enables it to undergo permanent deformation without elastic rebound, and without rupture. In order for a sediment to be very compressible or to have a high degree of cohesion it must be plastic within a certain range of water content.

Plasticity of cohesive sediments is due almost exclusively to the interaction between water and tabular particles less than 2 microns in size.^{4/} No mineral sediments exhibit plasticity that are composed exclusively of particles larger than colloidal size (see glossary). However, plasticity is a property of only a few minerals. For example, quartz ground to colloidal size will exhibit no plasticity at any water content or any degree of fineness of the particles. The clay minerals all possess some degree of plasticity.

The plastic range of a clay increases as the percentage of < 2 micron size clay minerals increases. The greatest range of moisture content between the plastic limit and the liquid limit occurs in montmorillonites. Mineralogical composition is the most important factor in plasticity as it controls the size and shape of the particles. Internal crystal structure causes montmorillonite to form in thin plate-like particles as small as .02 microns. The myriad minute particles have a large specific surface to adsorb and absorb water. Furthermore, the montmorillonite flakes are weakly bonded to each other. Not only the tiny flakes, but also the component sheets of the flakes having thicknesses of as little as 10 Angstrom units can separate and allow water and chemicals in solution to enter.

A montmorillonite rich in sodium ions has been determined to have a liquid limit of 700 and a plastic limit of 93 thereby giving it a wide range of plasticity, that is, a plasticity index of 607 percent. This example may be used to illustrate how the ion-exchange capacity of a clay mineral affects the range of plasticity. For instance, if the sodium ions in this montmorillonite are replaced by calcium ions, the liquid limit can be reduced from 700 to 124 and the plastic limit from 93 to 72, thus altering the plasticity index from 607 to 52.

Plastic clay materials can be very difficult to handle with ordinary construction equipment when they contain appreciably more than optimum moisture. Plastic clay soils that are very wet might not be usable since they are difficult to dry out.

Consolidation

Consolidation is (1) the deformation of a soil, upon being loaded, because of expulsion of water and/or a rearrangement of the soil particles which reduces porosity. In geology, consolidation is (2) any or all of the processes whereby loose, soft or liquid earth materials become firm and coherent (AGI,1). The first definition is appropriate in soil mechanics and is the one we are concerned with here in considering engineering properties. The term compressibility refers to the relationship between the increase of the unit load on a laterally confined soil and the corresponding decrease of its void ratio (Terzaghi, 30). Thus, compressibility is a function of porosity or void ratio.

In saturated soils of any type, since water is considered virtually incompressible, a change in volume must be accompanied by the intake or expulsion of water. In clay soils, because of low permeability, water moves

^{4/} Terzaghi 30, p. 566 and table II

very slowly and, temporarily, a saturated clay may appear incompressible. It should be recognized that soil compressibility depends on the extent to which the material will eventually change volume under static loading. Clay loses water slowly under load; settlement is gradual, and occurs over a long period of time. Thus, most clay materials are considered to be relatively compressible. A saturated montmorillonite would experience the greatest reduction in volume, illite intermediate, and kaolinite the least of the three groups of clay minerals.

Soil compressibility is mainly of concern because of the possibility of settlement of structures. If the soil beneath a structure contains layers of sand or stiff clay alternating with layers of soft clay, the compressibility of the sand and stiff clay can be disregarded, but not the compressibility of the soft clay. A foundation composed of deep saturated plastic clay would experience the greatest settlement upon application of a load. Because clay is very slowly permeable this foundation might continue to consolidate for several years. In contrast, gravel and sand compress very quickly because of their high permeability and the amount of consolidation or settlement is comparatively small.

The compressibility of layers of clay depends mainly on two factors: (1) the nature of the clay, and (2) the maximum load that has acted on the clay since its deposition. Imposition and subsequent removal of a load, p , on a sediment permanently reduces its compressibility under loads that are smaller than p . Therefore, a distinction is made between normally consolidated and pre-compressed or pre-consolidated sediments. Examples of a pre-consolidated sediment are: (1) those that previously were loaded with superimposed sediments that later were removed by erosion, (2) sediments formerly covered by glaciers, and (3) sediments compressed through desiccation. Normally consolidated sediments result from settling caused by gravity and continued deposition over them, but have never been subjected to a load reduction.

Shear strength

Shear strength is the internal resistance offered to shear stress. The shear strength of a clay material consists of two components -- cohesion and internal friction. The cohesive strength of clay material is by far the more important and varies widely according to many factors.

There are four principal factors that affect the cohesive strength of a clay soil; they are (1) water content, (2) type of clay mineral, (3) the proportion of clay to the sand and silt in the soil, and (4) the effect of the grain size of the sand or silt particles mixed with the clay. The most important of these is the water content which, as it increases, decreases the cohesive strength (Figure 14). At a given water content illite has more strength than kaolinite, while montmorillonite is relatively stronger than either. This relative cohesive strength is on the same order of magnitude as the cation-exchange capacity of these clay minerals. In the liquid state a clay material may have no shear strength whereas a stiff clay (i.e., below the plastic limit) will have a shear resistance exceeding its cohesive strength which is very high. The cohesive strength of clay materials often

can be increased by applying and maintaining loads long enough for consolidation to occur.

The cohesive strength of clay soil with given water content increases as the grain size decreases. Conversely, the strength decreases with the admixture of silt and sand-size particles, both as the proportion of sand or silt to clay increases and as the size of the silt and sand increases (Trask, 32). In other words, the cohesive strength of clay soils increases as the ratio of clay to sand is increased for all the clay minerals. A much smaller amount of montmorillonite clay in a clay-sand mixture is required to give the same strength as pure clays of other types; for example, a mixture of 90 percent sand and 10 percent bentonite has about the same strength as kaolinite or illite in a pure form. It has also been found that fineness of sand in the soil mass has influence on strength. The shearing strength increases with decrease in sand-grain size below 2 mm. Above this diameter size appears to cause little change in strength.

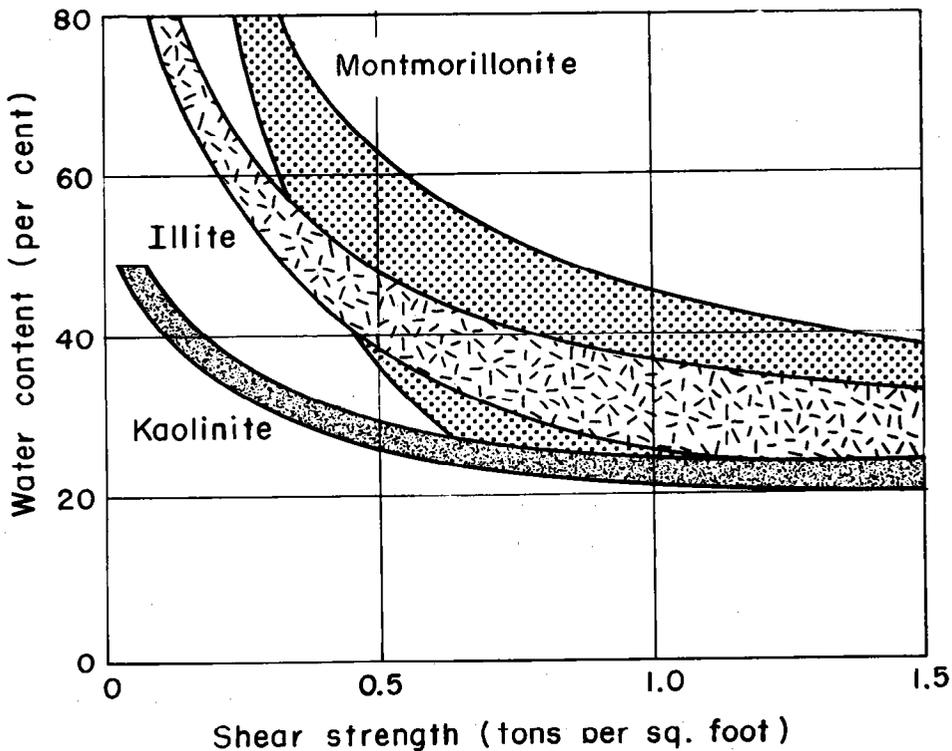


Figure 14. Relation of the shear strength of 3 clay minerals to water content.

Silt-size particles, in their intermediate position between clay-size and sand, frequently exhibit characteristics of the finest or coarsest constituents. Except for some loessial and lacustrine deposits, soils that are almost entirely in the silt-size range are rare. Normal or active clays that form as little as 2% of the mass can provide a great deal of strength. Where silts are non-plastic their strength can depend on the degree of consolidation. When sand particles greater than about .2mm form an important part of the soil mass, the strength is decreased.

The increase in strength for given water content with increasing content of fine-grained particles or increasing clay concentration is due to the greater surface area of the finer particles. With increased surface area the relative content of bound water increases resulting in greater shear strength.

Activity of clay materials.-- In a particular stratum of clay materials the ratio of the plasticity index to the clay fraction^{5/} content is approximately constant and has been defined (Skempton, 27) as the "activity" of the clay. The cohesiveness of soil samples can be compared by determining the activity which = $\frac{\text{plasticity index}}{\% \text{ clay fraction}}$. The greater the activity of a clay material the greater the contribution of cohesion to the shear strength. When the activity of a clay material is less than 0.75 the constituent clay minerals are said to be inactive. Normal clay materials are in the activity range between 0.75 and 1.25 and active clays have a ratio greater than 1.25. It has been found that kaolinite has the lowest activity, whereas illite is in the normal activity range. Clay materials with organic colloids and montmorillonite, as illustrated by bentonite, are active or highly active. The activity range between 0.75 and 1.25 includes the largest group. These are generally marine and estuarian clays and the dominant clay mineral is illite.

The most common constituents of the clay-size fraction were found by Skempton (27) to have the following activity values:

Quartz	0.0	Illite	0.90
Calcite	0.18	Ca- Montmorillonite	1.50
Muscovite (mica)	0.23	Na- Montmorillonite	7.2
Kaolinite	0.33, 0.46		

The increased moisture and decreased density associated with the expansion of montmorillonite clay soils tend to reduce the shearing strength of these soils. Under very light load conditions the shear strength of these soils can be reduced to practically zero upon saturation even though these soils may have fairly high strengths at moderate moisture conditions.

^{5/} Defined by Skempton as the percentage by weight of particles finer than 2 microns.

Most of the shearing problems are associated with silt and clay. These soils can contain a relatively high percentage of sand and still retain the characteristics of fine-grained soils. Granular soils usually cause the least difficulty as their shear characteristics can be determined or even estimated with considerable accuracy from their angle of repose which indicates internal friction. For reliable results of shear tests performed in the laboratory on clays, silts and intermediate soils the anticipated field conditions should be duplicated as closely as possible. The shearing resistance of soft, normally consolidated, cohesive material in the undisturbed state may be estimated from the results of vane shear tests performed in place when the soil moisture content is also determined.

Sensitivity

The sensitivity of a cohesive sediment such as a clay is equal to the ratio between the unconfined compressive strength of the material in an undisturbed and in a remolded state. Its value may range from 1 (insensitive clays) to more than 16 (quick clays). The sensitivity of a clay is greatly influenced by the field moisture content. When a sensitive clay is remolded it loses a great deal of its unconfined compressive strength that was previously acquired by thixotropic hardening. (The property of a fluid to gel upon standing. This change is reversible when gel is agitated). The strength that can be acquired by a sediment as a result of the thixotropic hardening depends on the prevalent clay mineral. It is smallest for kaolinite, intermediate for illite, and greatest for montmorillonite (Skempton and Northey, 28). This indicates the greatest sensitivity will be found in montmorillonite clay with high field moisture content. Most of the sensitive clays (having values of 4 to 8), extra sensitive (8 to 16), and quick clays (greater than 16) belong to one of two categories --- (1) glacial lake clays, and (2) marine clays which were subsequently lifted above sea level and lost their salt content by leaching (Terzaghi 30).

Expansibility ^{e/}

Knowledge of the expansion properties of clay materials is of great importance in the design of hydraulic structures because of the problems associated with volume change as the clay materials become saturated. These problems include uplift pressure, differential uplift and loss of shear strength of materials in the foundation of hydraulic structures.

There is a simple test for estimating swelling properties. This test consists of slowly pouring 10 cc of dry soil passing the No. 40 sieve into a 100 cc graduate filled with water and noting the increased volume of the soil after settling at the bottom. The free-swell value in percent equals

$$\frac{\text{final volume minus initial volume}}{\text{initial volume}} \times 100.$$

A commercial bentonite may have a free-swell value of 1200 to 2000 percent. Soils having free-swell values as low as 100 percent may have significant volume change when wetted under light loadings and should be treated cautiously. Soils having free-swell values below 50 percent seldom experience appreciable volume changes, even under loads as small as 1 psi.

^{6/} After Holtz, W. D., and H. J. Gibbs, Engineering Properties of Expansive Clays, reference 11.

The following laboratory determinations also give good indications of the expansive properties of clays when considered together:

1. The colloid content can be obtained from the gradation test. The colloid size fraction is the part most capable of contributing to expansion.
2. The plasticity index (PI) is an indication of expansion because the ability to hold various amounts of water in the voids and between the clay mineral layers can allow change in total volume. High plasticity indexes are necessary in order for a soil to increase volume significantly in progressing from the solid toward the liquid state.
3. The shrinkage limit is that moisture content in percent of dry weight at which further loss of water by evaporation causes no reduction in volume. The shrinkage limit is the lower limit of volume change. A low shrinkage limit indicates that a soil can begin volume change at low moisture content.

The montmorillonite clay minerals swell when wetted by water, while the illite and kaolinite groups do not swell or swell to a considerably less degree. Therefore, the amount of swelling to be expected in a soil is essentially dependent on the amount of montmorillonite present and the kind and quantity of exchangeable ions.

Dispersibility

Dispersibility refers to the water stability of clay aggregates; in other words, to the tendency of clay aggregates to break up or slake when saturated with water. It is due to the progressive swelling and sloughing off of the outer layers. The SCS dispersion test is a measure of the amount of <.005 mm clay that slakes into suspension without prolonged mechanical agitation or chemical dispersants. Critical values are 25% or more. Dispersed conditions may indicate excessive settlement, piping or erosion. Montmorillonite has a greater tendency to go into suspension than other clays because of the smaller particles and greater negative electrical charge per weight of particle repelling one from the other.

Other

There are other properties affecting engineering uses of clay materials that may require investigation such as: desiccation accompanied by cracking, and the phenomenon of frost heave where a clay surface is unprotected.

Identification

Recognizing the role various clay minerals play in determining the engineering usefulness of cohesive soils, the advantages obtainable from identifying the three main groups of clay minerals begin to be seen.

There are numerous ways of identifying the clay minerals but no one of them seems to be complete. Each of the tests reveals certain characteristics of the clay mineral and a combination of several tests permits accurate determinations. Unfortunately, most of the means of identification require complex techniques, expensive equipment and skilled specialists.

The composition of the clay mineral sample is usually complex and requires more than one of the following tools to establish the nature of the minerals and their relative amount: the petrographic microscope, chemical analysis, dye adsorption, determination of cation-exchange capacity, X-ray diffraction, infrared absorption, the electron microscope and differential thermal analysis.

Petrographic investigations usually only provide guidance for further tests. Chemical analyses, and particularly the determination of cation-exchange capacity, are helpful but often provide only supplementary information. Dye adsorption provides at times strong indications but it is rarely conclusive. X-ray diffraction leads to an understanding of the structural characteristics of the clay mineral. Infrared absorption has limited usefulness but as more knowledge is gained in this field is becoming a more important adjunct to other tests. The electron microscope is a powerful tool in clay mineralogy but involves a very special technique and requires expensive equipment. Differential thermal analysis reveals information on the behavior of clay minerals and many times, but not always, permits identification. For additional information on these identification techniques see *Clays and Clay Technology* (4).

All of the tests discussed above are performed in the laboratory. However, the dye adsorption or staining tests have some limited application as field tests. Some of the staining tests have been tried on clay materials by SCS personnel in the field with varying accuracy in estimating clay mineral content. Three of the stains used were aqueous benzidine, malachite green in nitrobenzene and gentian violet in nitrobenzene. All of the samples must be treated with hydrochloric acid first. These tests give reactions as follows:

Benzidine test *

A saturated water solution of the organic compound benzidine (or benzidine hydrochloride) which is slightly pink will produce a purple-blue purple on montmorillonite. No color reaction takes place with kaolinite. Illite will develop hues of blue (Mielenz and King, 19).

Malachite-green test

The staining agent used is a saturated nitrobenzene solution of malachite green. Clay minerals of the kaolinite group merely adsorb the dye, becoming blue to green-blue after application of this solution. Montmorillonite becomes yellow-red and illite becomes purple-red purple (Mielenz and King, 19).

Gentian (crystal) violet test

The test solution is 25 cc of nitrobenzene and 0.1 gram of gentian violet. This staining solution causes montmorillonite to appear green at first and then change to a greenish yellow or orange yellow. Illite becomes dark green while kaolinite merely adsorbs the dye.

Mielenz and King (19) have found the three best indicators of clay minerals through dye adsorption to be (1) benzidine, (2) nitrobenzene with malachite green and (3) nitrobenzene with safranin Y.

* Do NOT use this test. BENZIDINE MAY BE HAZARDOUS TO HUMAN HEALTH.

Safranine Y test

The staining agent is saturated nitrobenzene solution of safranine (a mixture of $C_{21}H_{21}N_4Cl$ and $C_{20}H_{19}N_4Cl$). In this test acid-treated montmorillonite develops purple-blue hues, illites become purple-red purple to red. Kaolinite merely absorbs and adsorbs safranine Y becoming red to red-purple red.

Two types of reaction form the basis of the identification of clay minerals with staining tests. The first type is an oxidation-reduction reaction in which certain aromatic amines are partially oxidized producing characteristic colors. The water solution of benzidine is of this type.

The other stain tests previously mentioned are acid-base reactions in which stains act as indicators of pH in adsorbed water films. Clay samples should be acid-treated and objectionable materials removed before making stain tests. The two types of tests are complementary. For more details on procedures, applications and limitations, refer to Mielenz and King (19).

Summary

Classification

Clay minerals are divided according to structure into amorphous and crystalline categories. The latter is subdivided into two layer, three layer, mixed layer and chain structure clay minerals.

The origin and occurrence

The clay minerals are formed in two principal ways: (1) As alteration products due to hydrothermal action, and (2) by weathering processes. Clay minerals formed by weathering processes are more common and important. The clay minerals produced by weathering are determined by the parent rock, climate, topography, vegetation and length of time involved.

Kaolinite seems to require an acid environment from which Ca, Mg and Fe are removed; montmorillonite requires an alkaline environment in which magnesium and iron are present. Illite is especially common in marine sediments and requires an alkaline environment with Ca, Mg, ferrous iron and potassium present. Clay minerals can be weathered or further altered by a change of environment.

The structure, shape, size and density

In summary, we may say the principal clay minerals generally break down to particles 0.002mm (2 microns) in size or smaller and fall into four types regarding internal crystalline structure: two layer, three layer, mixed layer, and chain structure. The first two are most important and most common. These layers ideally are composed as follows: One of silicon and oxygen atoms in regular tetrahedral arrangement with these tetrahedrons linked together forming a hexagonal network; the other of aluminum and oxygen in octahedral arrangement. These layers are tied together chemically in alumina-silica pairs as in kaolinite or in silica-alumina-silica trios, as in montmorillonite and illite.

A clay mineral is most likely to be a hydrous aluminum silicate, but may vary considerably both in physical properties and chemical composition. The clay mineral particles are commonly flake shaped with a tendency to be six sided, but may also take the form of laths, fibers, tubes and sub-rounded flakes, or even be somewhat spherical. They vary in size from a minimum dimension of 20 Angstrom units (.002 microns) approaching unit molecular cell height in some tiny particles of montmorillonite, to dickite flakes with a maximum dimension of 8 microns. The dry density or specific gravity of clay minerals varies between 2 and 3 grams per cubic cm.

Ion exchange

The cation-exchange reactions are very important properties of clay-minerals and should be considered by field technicians.

Factors to be considered as influential in cation exchange revolve around such variable conditions as exchange-capacity, causes of exchange, rate of exchange, environment of exchange reaction, reduction of exchange capacity, and the nature of the ion.

The clay-water system

The special relationship between clay minerals and water give the clay-water system properties which are unlike those of coarser soil materials.

The water in clay materials consists of (1) pore water that can be removed by mechanical force, (2) water that can be removed by heating to 110°C, and (3) remaining water which is in a solid state and firmly bonded to the clay particle or else is a part of the lattice structure of the mineral.

The polarity of water and its orientation with the platy clay mineral particles is fundamental in the development of plasticity.

The heat evolved by a dry clay mineral on wetting is comparable to its exchange reaction capacity.

The compression strength of a remolded dry clay material with water added has a tendency to increase on standing without any further change of water content.

Properties of clay materials as related to engineering uses

Engineering properties refer to the properties of a material that influence its performance during and after construction operations. The following properties of clay materials were considered:

1. Porosity of clays may range from about 20 to 85 percent or in terms of void ratio the variation would be 0.25 to 5.7. Clay soils as a class have greater porosity than soils composed of larger particles.
2. Permeability of clay materials is influenced not only by the size and amount of void space and interconnections, but also by the cation-exchange capacity. The Soil Mechanics Laboratory usually reports permeability in ft./day which for clays is in the neighborhood of 2.8×10^{-5} ft./day. The Corps of Engineers uses cm/sec. which for Cl and CH is about 10^{-6} to 10^{-8} cm/sec.

3. Plasticity in soils is a property of clay minerals, and the plastic range increases as the percent of colloidal size clay minerals increase. Montmorillonite being composed of the smallest particles, exhibits greatest plasticity. Plasticity is the primary property used in distinguishing fine-grained soils for engineering purposes.

4. Compressibility of clays depends on the nature of the clay and the maximum load that has acted on the clay since its deposition. Under similar conditions of environment a CH would be more compressible than a CL. Clay is compressible, increasingly so with greater water content, but because of low permeability the rate of consolidation is slow. A clay under load may consolidate for a period of months or even years.

5. Shear strength of a clay depends on its cohesive strength which varies some with particle size, but chiefly with water content. As the moisture content of a clay is increased the shear strength is reduced.

6. Sensitivity is the ratio of the unconfined compressive strength of an undisturbed clay to that of a remolded clay. Most of the sensitive clays (sensitivity over 4) are glacial lake clays or marine clays lifted above sea level and leached of their salt content.

7. Expansibility.-- The montmorillonite clay minerals swell when wetted while the illite and kaolinite groups do not swell or swell to a considerably lesser degree. The amount of swelling to be expected in a soil depends mainly on the amount of montmorillonite present and also the exchangeable cations.

8. Dispersibility.-- Montmorillonite has a greater tendency to go into suspension than other clay minerals because of the smaller particles and greater negative electrical charge per weight of particle repelling one from the other.

Identification

Usually more than one test is required for clay mineral identification and the tests require laboratory facilities. However, at times, estimates of the clay mineral groups involved can be made in the field with rudimentary staining tests. Color reactions of montmorillonites, illites and kaolinites are discussed using the benzidine, malachite green, gentian violet and safranin Y tests.

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