Soil Stabilization and Colloid Science

ERNST A. HAUSER, Professor of Colloid Science,
Massachusetts Institute of Technology

Introductory Remarks by the Chairman: A great problem is to scientists like a medieval fortress to beleaguering soldiers. The walls are scouted for weaknesses, and effort is concentrated on what is considered to be the weakest spot. If a breach is made, most of the men will use it to enter the fortress. A scientific pioneer, as any other pioneer, does not like crowds. Even though he had originally recognized the weakness and was the first in the breaching of the wall, he will leave the crowd now seeping through in order to attack other problems and break new walls.

Hauser is such a true pioneer and a worthy representative of colloid science, a discipline that is always out in front in attacking complex problems and that leaves the conquered country to be organized by her socially more-accomplished sister, physical chemistry. Hauser is well known all over the world for his pioneering accomplishments in colloid science and its application to the chemistry and technology of rubber and other clastomers and of clays and other silicate minerals. His many contributions to science and technology are too numerous to even list in this place; several of these were of prime military importance during the Second World War.

It is gratifying that Hauser consented to enrich this symposium with an interpretation of the relations between soil stabilization and colloid science.

● COLLOID science is always needed in order to explain the interaction of matter present in the colloidal range of dimensions with other substances. Any substance, organic or inorganic, falls within the colloidal range if it is present in at least one dimension in the range between one micron and one milimicron.

In soil stabilization, clays must always be considered as very important and often determinant soil components; therefore, a sound knowledge of their structure, composition and morphology is of great importance.

A vast amount of information on clays has been accumulated since 1925, when it was possible, for the first time with the aid of new research tools and the formulation of new concepts, to embark on a truly fundamental study of clay minerals. This gigantic work has resulted in a good, though still not complete, understanding of the occurance, composition, and colloidal properties of all clay minerals (1).

This contribution will cover the most-important facts of the colloid science of clay minerals and the most-recent concepts pertaining to them. Despite the emphasis placed here on the clay minerals and their properties, it should not be overlooked that clay minerals in natural soils frequently have adsorbed on their surfaces organic matter resulting from the decomposition of plants or animals. For this reason, the surface activity of these clays will differ pronouncedly from that of pure clay.

This condition has been aptly described by Winterkorn (4) as follows: "Clay minerals in natural soils are not as clean as a scraped bone; rather the mineral surface is normally in as close a relationship with adsorbed and synactive organic matter as a bone in a living being is with cartilage and muscle tissue." Also, microörganisms are normally present in natural and often in stabilized soils. Their bearing on soil stabilization has been recognized by only a few workers in the field (5). An explanation of the variability in properties of clays will be offered before the influence exerted on soil stabilization by organic matter is discussed.

Genesis of Clay Minerals

Of all the theories pertaining to the origin of clay minerals, geologists and mineralogists have largely accepted the "residual clay" and the "transported clay" theories. The former is based on the assumption that the formation of clay minerals is the result of surface weathering of fresh rocks or is due to the action of solutions. From a colloid-scientific point of view this theory deserves special attention. However, it does not offer a truly

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satisfactory explanation of the genesis of the two basic components of clays, silica gel, and alumina or magnisia gel.

Although some of the latest contributions to the chemistry of silicates admit that colloid science plays an important role, the majority of scientists interested in the colloid science of silicates are seemingly still not familiar with the fact that colloid science had already made basic contributions to the theory of the genesis of silicates over a quarter of a century ago (2).

Even as early as 1779, research was done in the field of what is known today as the colloid science of siliceous matter. In his paper, "De Terra Silicea," the Swedish scientist, Torbern Bergman, stated:
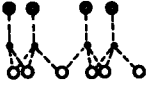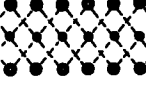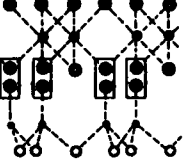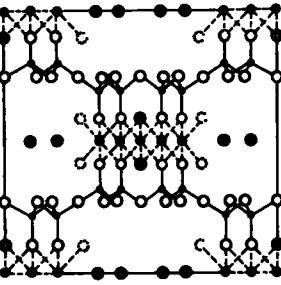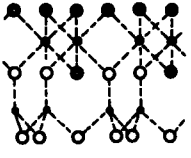
"Finally I must still think of those incomplete phenomena which depend on a seeming solubility. This siliceous liquor (alkali silicate solution--E.A.H.) is precipitated by all acids, because the alkali prefers to hang onto them rather than to the gravel. This precipitated gravel has a very expanded and loose texture and is filled with water, so that it is twelve times as heavy when moist than when dry. If more water is added before adding acid, however, the solution remains clear, even if more acid is then added than would be needed to neutralize the alkali. This is a peculiar phenomenon and the reason for it is probably the following: Through the dilution with water the siliceous particles are very 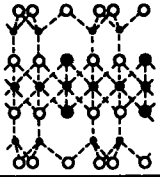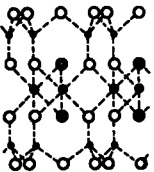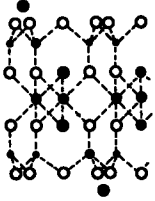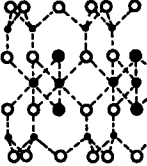much separated from each other, or made finer and better distributed throughout the liquid. Although the particles should settle out, being heavier than liquid, they cannot in this case overcome the resistance due to friction, because a greater force will be needed to accelerate sedimentation than that resulting from the difference in specific gravity. The silica particles remain suspended in the liquid but at the same time are invisible due to their fineness and transparency."

The more-modern work which has been overlooked dates from 1927, when the German geologist, Schornstein, made a fundamental contribution to the colloid science of siliceous matter. The following is a passage from one of his basic papers (2):

"During the decomposition of silicates the following must be borne in mind: In the magma, silicic acid is in chemical equilibrium with the bases. It is able to form complex molecules which, however, are chemically well-defined; this is demonstrated by the fact that all these silicates are capable of separating into crystallographically well-defined particles. Silicic acid owes this property to its high acidity at elevated temperatures. At low temperatures the acidity of silicic acid is so small, however, that it can form a salt only with the strongest bases, as for example Na_2O and K_2O. It will be precipitated from these by the weakest acid, however, even by water alone. This implies that most of the silicates are present in a metastable equilibrium, even at normal temperatures. When water decomposition sets in, the equilibrium is disrupted. In the absence of acid, oxides or hydroxides of the silicate bases are formed and silicic acid is liberated. In the presence of carbonic acid, humic acid, or sulfuric acid, primarily those bases will be attacked which will form soluble salts with these acids. The moleculer structure of the silicate is disrupted and at certain locations of the crystal lattice the acid-insoluble bases and silicic acid remain. When liberated they are present in a molecular disperse condition. Since they are insoluble, they are not capable of forming a molecular solution with water; oversaturation results, causing polymerization. This can either occur in space-lattice fashion, resulting in the formation of crystals, or, if the oversaturation is too great in comparison to solubility and the ability to crystallize too small, colloidal gels are formed. The formation of colloids due to the decomposition of the silicate is a condensation reaction."

We still have no truly satisfactory answer to the question of how clay minerals were actually formed or how their genesis can be explained in a way which takes into account all the knowledge now at our disposal. Many years ago the alteration of pure silica and alumina to kaolinite or montmorillonite was demonstrated. In all probability we are dealing here with a combination of the chemical reactions attendant upon leaching and a devitrification of the glass, the reaction then proceeding through a hydration and adsorption of ions. In all probability the silica and alumina gels reacted first to form halloysite; then, by condensation, kaolinite or montmorillonite, talc, mica, and other minerals, depending on the ions present. In any event, clays

The schematic drawing in the first column of each section represents the composition of the unit cell of the respective building unit or complete crystal lattice. All atoms have been projected into one plane. The second columns give the number and type of atoms or groups for every lattice plane. 1 = silicon tetrahedron, 2 = aluminum octahedron, 3 = magnesium octahedron, 4 = hydrated silica, 5 = gibbsite; 6 = brucite, 7 = halloysite; 8 = attapulgite; 9 = kaolinite, 10 = talc, 11 = nontronite, 12 = mica (illite); 13 = montmorillonite (substituted)

Figure 1. Structural data of the most-important clay minerals and their building units.

owe their genesis to the presence of silica and alumina or magnesia gels and the changes they undergo with time or temperature (1, 2, 3).

A fact which until quite recently has not found the attention it deserves is that, in spite of the inertness of most siliceous matter, the chemical reactivity of the silica surfaces surpasses that of most stable oxides. Systematic research on the surface chemistry of silicates has led to the discovery of unexpected chemical reactions which result from the dehydration or polymerization of silicic acid (2).

Structure of Clay Minerals

In 1923 Hadding and, a year later, Rinne were able to prove by X-ray-diffraction studies that clays are not composed of matter in the amorphous state, as had been assumed, but that they are crystalline in structure. Since then our knowledge of the structure of clays has been greatly increased. Colloid science has offered a better understanding of some of the phenomena which are so characteristic of clays and which could not be explained by physico-chemical reasoning alone.

Bearing in mind the fact that all clays are composed of silica and alumina or magnesia, and first taking the unit cells of these components into consideration, it will immediately be realized how these structures can increase in dimensions. It will then also be seen how they can combine to form either simple double layers or triple layers of silica and alumina or magnesia (Figure 1).

A silicon atom binding four oxygen atoms forms a tetrahedron; the radii and distances between the silicon and oxygens permit the four oxygens to touch, leaving a cavity just large enough to include the silicon (Figure 2, left).

The second building unit is a combination of aluminum with six oxygens, where the latter completely enclose the aluminum atom (Figure 2, right). The aluminum can be exchanged for magnesium, but since magnesium is a larger atom it does not fit exactly into the cavity; therefore, a slight strain in the structure is set up. These two combinations are known as aluminum-oxygen and magnesium-oxygen octahedra.

These building units are held together by the sharing of electrons. Since each silicon atom can share four of its outer

electrons, whereas each oxygen atom needs two electrons for saturation, a silicon-oxygen tetrahedron is unsaturated, lacking four electrons. If the oxygens are replaced by hydroxyl groups, however, the system is saturated, since the missing electron has been supplied by the hydrogen of the hydroxyl group.
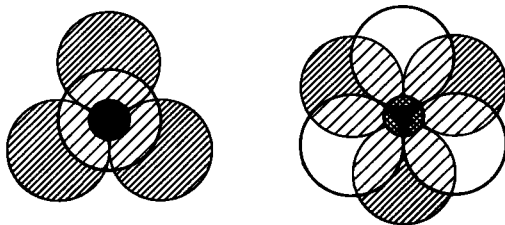

Figure 2. Left: A silicon-oxygen tetrahedron (schematic). The oxygen atom on top has been drawn as a transparent sphere to show the location of the silicon atom in the cavity formed by the four oxygen atoms. Right: An aluminum- (magnesium) oxygen octahedron (schematic). The oxygen atoms constituting the upper layer have been drawn transparent to show the location of the aluminum (or magnesium) atom in the cavity formed between the oxygen (hydroxyl) layers.

Starting with orthosilicic acid we find that in forming a silica sheet every oxygen atom located in one plane is shared by two silicon atoms, except the oxygens located at the edges of the sheet, which remain unsaturated; the oxygens in the vertex position of the tetrahedra have a hydrogen attached. This structure is saturated, therefore, and is known as a hydrated silica sheet (Figure 3). If we join nonhydrated silicon tetrahedra to form such a sheet, we find that all oxygen atoms are saturated except those in the vertex, edge, and corner positions. Consequently, any unsaturation occuring due to edge or corner positions of atoms will be negligible compared to the surface unsaturation of such a structure.

The second building unit--the aluminum or magnesium octahedron--is capable of forming similar sheets. Assuming that all the oxygens are saturated by hydrogen, then two layers of hydroxyl groups, each in close hexagonal packing, can be cemented together by magnesium atoms, so that six hydroxyl groups share three magnesiums. Except for edges and corners, such a sheet is saturated and neutral. Several of these composite layers can be held together by

secondary forces, such as van der Waals' forces.

It is interesting to note that by cementing two of the hydroxyl sheets together with magnesium, the high symmetry of a hexagonal configuration is disturbed and reduces to a monoclinic one, since the hydroxyl sheets are staggered. The mineral built up according to the above structure is known as brucite (Figure 1).
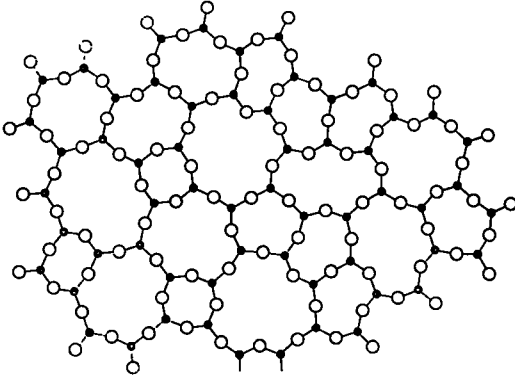

Figure 3. Structure of an unsymmetrical silicon-oxygen sheet; silica glass (schematic)(after W. H. Zachariason).

If aluminum replaces the magnesium in the octahedral sheets, changes have to be made in order to retain a neutral sheet. Aluminum can share three electrons, magnesium only two. Consequently, one third of the places formerly occupied by magnesium must remain vacant. Therefore, the aluminum octahedral sheets will not be so densely packed as the magnesium octahedral sheets. This mineral is known as gibbsite.

Just as silicon-oxygen tetrahedral sheets are built up from single silicon-oxygen tetrahedra, gibbsite from the aluminum-oxygen octahedra, and brucite from magnesium-oxygen octahedral sheets, the minerals of the kaolinite, montmorillonite, and illite groups are built up by joining gibbsite or brucite sheets to silicon-oxygen tetrahedral sheets (1).

Some Colloid-Scientific Considerations

According to its crystallographic classification, kaolinite is a monoclinic system which displays good cleavage. In the formation of fragments the fracture occurs along the basal cleavage plane and also normal to it. Fracture along the cleavage plane does not rupture primary valence

bonds, and this results in the formation of thin hexagonal platey particles. If the fracture is parallel to the c axis of the crystal, however, the bonds between Si and O, Al and OH, or O must be broken. These broken bonds are the basis for the preferential adsorption of hydroxyl ions. The adsorbed hydroxyl ions are hydrated; that means that they carry with them water molecules which become part of the water hulls. The particle and the cations located close to it constitute the Gouy-Freundlich diffuse double layer.

If a small trace of an electrolyte, e.g., sodium hydroxide, is present, profound changes in the forces connected with the micelle will occur as a result of the preferential ion adsorption on the particle. This results in the setting up of a considerable repulsive force at the edge of the lyosphere. The charge density on the particle and its potential are high, and from a colloidal point of view the particle is at maximum stability. In this state the kaolinite slip is deflocculated or dispersed.
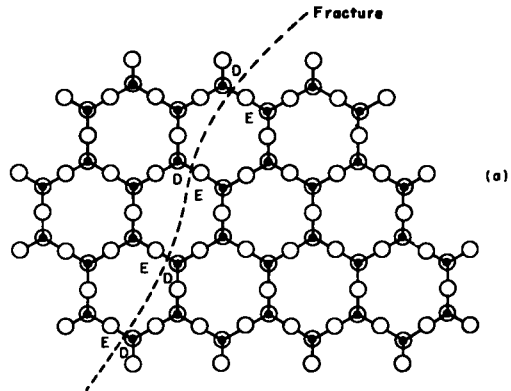
Figure 4. The formation of E units and D units at the fracture surface of crystalline SiO_2 (after W. A. Weyl).

If we now look at the structure of a clay mineral of the montmorillonite group, we find that these substitutions result in establishing net residual negative charges on certain sections of the lattice, which in turn cause attraction. Sodium is the most common cation found in naturally occurring montmorillonites. The crystal units of montmorillonite are held together quite loosely by weak O-O bonds. The sodium ions are primarily adsorbed on the surfaces of the silica sheets and to a negligible extent on the fracture along the c-axis. When hydration occurs these ions pry the

particles apart and a double layer of appreciable thickness is formed. Montmorillonitic clays thus exhibit a high degree of swelling (6).

Silica in its various modifications represents a three-dimensional network of SiO_4 tetrahedra in which the O^{2-} ion is shared by two Si^{4+} ions.

In the interior of silica the building unit is the Si^{4+} $(\frac{O^{2-}}{2})$ group. In contrast thereto, two types of groups must be expected in the surface, namely Si^{4+} $(\frac{O^{2-}}{2})3$ and Si^{4+} $(\frac{O^{2-}}{2})3 O^{2-}$. The first, known as a deficiency unit, or D unit, shows an oxygen deficiency resulting in an excess positive charge; the second, known as an excess unit, or E unit, has oxygen in excess over the stoichiometric ratio and carries a negative charge (Figure 4) (2).

This may lead to an electron transfer from the E unit to the D unit so that the potential field is reduced and with it the energy content of the nascent surface. For silica such an electron transfer does not seem very probable, since this would lead to the formation of Si^{3+} ions having eight-plus-one outer electrons. It is the instability of this electron configuration which most probably excludes such an electron transfer from contributing to the stability of the nascent surface of silica.

This information indicates the complexity of the problems pertaining to the properties exhibited by clayey substances and demonstrates one phase of the importance of colloid science for soil stabilization.

In dealing with colloidal clays it is impossible to explain their properties by rigid mathematical laws, as so successfully applied in physico-chemistry. This should not imply that the use of any mathematics in this field is of no value at all; however, there is little to be gained by drawing conclusions based on mathematics alone, disregarding the peculiarities of the colloidal state of matter. The state involved in colloid science is characterized by a high surface-over-volume ratio. In accordance with the electronic theory of valency, an ion located in the surface of a particle must be far-more reactive than one in the interior. Therefore, matter present in the colloidal state must be much-more reactive than its chemical composition alone would indicate. This also explains why most of the properties characteristic of colloids cannot be harnessed into rigid mathematical concepts.

Ion Exchange

Of all the phenomena exhibited by minerals which form colloidal micelles when in contact with water, the most important is the ion-exchange reaction. This reaction was originally recognized by Thompson in his investigation of the properties of soils (2).

The ultimate clay crystal carries a net negative charge. This is the result either of anion adsorption onto its surface or of an unbalanced crystal lattice. Whatever the basic cause, the individual ultimate clay particle may be pictured as a very-complex anion. To balance the charge the particle will tend to adsorb the necessary number of cations available in the environment. These cations then act as the so-called counter ions. When dispersed in water they will hydrate to a degree depending on their valency and hydratability, dissociate to a certain extent from the surface of the particle, and thereby form a diffuse electric double layer, thus giving rise to the formation of a colloidal micelle. Such a clay particle may therefore be compared with a dissociated electrolyte, the size of one of its ions falling within the colloidal range of dimensions.

For example, just as a soap-like sodium oleate in hard water will exchange its sodium ions for the less-hydrated calcium ions, the counter ions of the clay particle will be exchanged with ions from the dispersion medium if the resulting micelle would have less tendency to hydrate and carry a lower charge, or both. This reaction is, of course, the more pronounced the more ions of a high degree of hydration are present in the clay under investigation. The magnitude of this ability to adsorb cations depends primarily on the structural configuration of the nucleus of the colloidal clay micelle. It is usually expressed in milliequivalents of cations per hundred grams of clay.

By the same reasoning, however, clays may also adsorb anions where net positive charges are set up in the crystal lattice or where the hydrogen of a hydroxyl group is exchanged for a stronger ion, like PO_4^{---}. Generally speaking, therefore, it may be stated that ion exchange will follow the Hofmeister or lyotropic series, at least

for cations, i. e., the higher the atomic weight of an ion, the more firmly it will be held by the exchanger. Therefore, the exchange reaction for monovalent ions will follow the series Li$<$Na$<$K$<$NH$_4<$Rb$<$Cs, and for bivalent ions the series Mg$<$Ca$<$

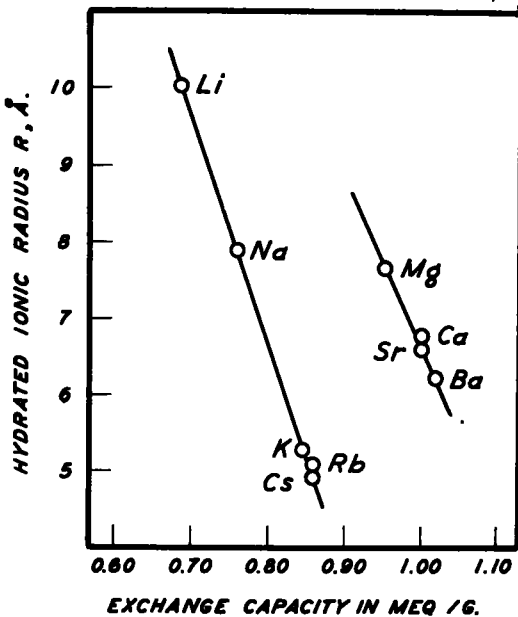

Figure 5. The radii of hydrated ions versus exchange capacity at equilibrium.

Sr$<$Ba$<$La (Figure 5).

There is one other fact which should not be overlooked, however. Besides valency and hydration, the size of the exchanging ion is also important; it is difficult to exchange with ions which have an apparent diameter of at least 2.64 Angstrom units, the diameter of the circle which can be inscribed within the hexagonal net of oxygen atoms forming the silica sheet. It immediately becomes evident why it is extremely difficult, if at all possible, to exchange with a potassium ion, which has an apparent diameter of 2.66 A. (Figure 6).

For a long time it was assumed that ion-exchange reactions were limited to inorganic ions. It has been shown, however, that organic ions can react in the same way (7). Organic constitutents of soils play a large part in the exchange capacity of normal soils and thereby influence the soil-water relationships. Bearing this in mind, it becomes clear that the exchange capacity of actual soils cannot be predicted from their mineralogical composition only, but that careful experimental research is

essential to obtain the correct information.

Soil Stabilization

The term "soil stabilization" includes all physical, chemical, electrical, thermal, and other methods by which soils can be improved to serve better their intended purposes (8). Stabilization has been achieved by the use of bituminous materials, especially for road and airstrip construction; much work has also been carried out with tars, asphalts, portland cements, lime, calcium chloride, sodium silicate, lignin derivatives, and various other natural and synthetic resins.

The problem of stabilizing soil is particularly important in dealing with fine-grained clays, most of which contain montmorillonite. In all these clays water will have a marked effect, since such soils lose their shear strength when very wet.
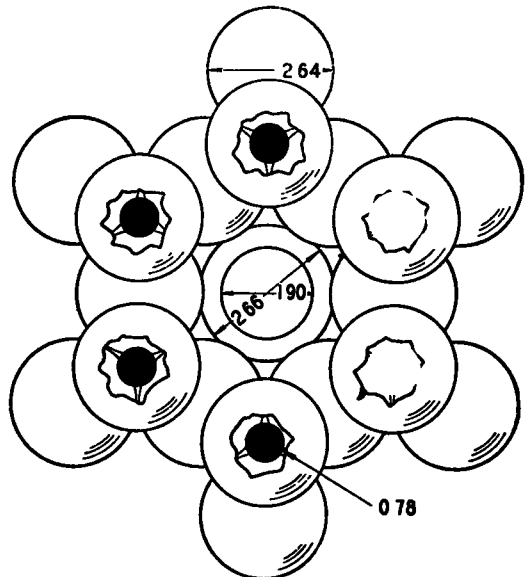
Figure 6. Hexagonal arrangement of silicon-oxygen tetrahedra in a silica sheet (schematic). The top oxygen atoms have been cut open to show the location of the silicon atoms. The large circle in the center space with a diameter of 2.66 A. corresponds to the diameter of a potassium atom, the smaller one to a sodium atom. The actual dimensions in Angstrom units (1 A. - 0.1 millimicron) for the different atoms are indicated on the drawing.

Most of the treatments now in use encounter increasing difficulties as the size of the dominant soil particles decreases.

For this reason, the search for better stabilizers for fine-grained soils is being pursued quite actively.

A primary military problem is to obtain an almost immediate improvement of the structural properties of naturally occurring soil. The treatment must be effective with various naturally occurring soils even if they differ pronouncedly in their water content, so that they will show an appreciable strength both in shear and in tension without being affected by water after they have been reacted. It must be possible to incorporate the stabilizer into the naturally occurring soil without actually removing the soil from the site; also, the stabilizer should be effective in very small proportions.

One approach toward the solution of this problem is the incorporation into the soil of a monomer which can be polymerized thereafter at normal temperature, thereby forming effective bonds or links with the soil as a basic part of the new structure.

The monomer to be employed must be able to enter into ion exchange with a base-exchangeable soil or to provide an effective bond with soils exhibiting no base-exchange properties. In the latter case the polymerized monomer will form long-chain polymers into which soil particles are interwoven.

The monomer should be ionizable and represent a water-soluble salt. If the organic part of the monomer is negatively charged, the cation of the monomer must be polyvalent, so that a positively charged complex monomer ion becomes available for base exchange with the negatively charged soil particles. Furthermore, a polyvalent cation is needed whenever the cation is to serve as a link in cross-polymerization.

It must also be borne in mind that a certain quantity of free soil water is needed when chemicals of this type are added to the soil, so that they become ionized and immediately enter into the exchange reaction. Generally it can be stated that most soils have enough water present to meet the requirements for polymerization. Any monomer which is not dissolved and base exchanged with the soil particles remains available for polymerization in the final phase of the treatment.

Most important is the formation of an insoluble polymer in which the soil particles become part of the polymer. If this is accomplished the permeability of the soil decreases, because a continuous soil-polymer-water structure is formed. The soil water is also held more closely to the soil structure by the formation of the polymer structure and its dipolar alignment.

On June 4, 1946, United States Patent 2,401,348 was issued to E. A. Hauser and E. M. Dannenberg for molding compositions using base-exchange solids like bentonites in finely divided form to which an ionizable salt of a polymerizable carboxylic acid was added. This compound contains the polymerizable olefinic group of the salt. In Claim 1 of the patent the use of acrylic acid salts was claimed specifically (2).

Although this patent did not refer to the use of a polymerization catalyst which would permit the reaction to take place at normal temperature, it must be considered, nevertheless, as the original idea for working out the acrylate and similar methods for soil stabilization.

Whenever a base-exchange solid like sodium bentonite is used, the reaction has to be carried out in such a way that the sodium ions which act as counter ions in the clay micelle may be exchanged, so that the clay becomes of the nonswelling type. As work continued it was found that salts of multivalent cations, e.g., lead acrylates, generally give satisfactory results.

As a result of this work a patent on "Stabilization of Soils" was granted in 1953 (2). According to this patent, the dissociation of calcium acrylate is accompanied by a base-exchange reaction in which the ionized calcium acrylate ions replace sodium ions associated with the soil particles.

After the soil has been intermixed with calcium acrylate and a base-exchange reaction has taken place, the soil-monomer mixture can be polymerized at normal outdoor temperature through the use of an appropriate catalyst, e.g., one comprising an oxidizing agent and a reducing agent.

Calcium acrylate will not ionize to an appreciable extent; therefore, a complex colloidal electrolyte forms. Calcium ions have a diameter greater than that of the "inscribed circle" (see Figure 6), which prevents their penetration of the silica layer of the clay particle; therefore, the calcium ion will be attached to the gibbsite layer of most clay particles. If a very-

moist soil is involved in the reaction, however, it becomes questionable whether this can be accomplished. In most cases, therefore, only a skeleton of calcium acrylate surrounding the soil particles will actually be formed and not a truly chemically combined structure.

What is still being widely overlooked today is the fact that, as previously mentioned, soils can never be considered as being absolutely pure; the presence of decomposed plants (which act as nutrients for bacteria) and of other microörganisms must be taken into consideration (4, 5). Therefore, any work carried out with pure clays or sands is only of theoretical importance (9). Far more attention must be paid to the reactivity of the different soils with their surrounding media to obtain truly successful results. Only to make tensile and shear tests on specially molded samples can never result in a truly satis-

factory answer to the problems involved in soil stabilization. Soils should first be subjected to systematic chemical and bacteriological investigation.

Without paying more attention to these factors, it will never be possible to stabilize soil in situ satisfactorily.

Conclusions

Colloid science is of extreme importance for any work pertaining to the problem of soil stabilization. For this reason the most-important facts pertaining to the structure of clay minerals have been discussed. On the basis of the clay structures, the colloidal properties of clays have been referred to with specific attention to the phenomenon of ion-exchange reactions. Based on this information, the application of acrylic resin exchangers is discussed and the problems involved in the use of calcium acrylate are pointed out.

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