

Organization of Water on Clay Mineral Surfaces And Its Implications for the Properties of Clay-Water Systems

RALPH E. GRIM, Research Professor of Geology
University of Illinois, Urbana

Introductory Remarks by Chairman

There was a time when every leading physical chemist had his own favorite picturesque expression of the Second Law of Thermodynamics. The advantage of such similes or parables was that they stimulated the imagination and were easily retained by the memory. Their disadvantage was, of course, lack of precision. As everything potent, they had to be used with caution. However, if properly employed, such formulations can be powerful agents for the progress of knowledge and understanding. In this class, falls the statement by Harkins that whenever two different materials are in contact, an interface structure will be formed in such a manner as to make the transition from one material to the other the least abrupt possible. In the present symposium, we are vitally interested in the structure of the interphase between liquid water and solid mineral—especially clay surfaces. Proceeding from the better known to the lesser known, we may and should approach this interphase not only from the water side but also from the mineral side. It is, therefore, appropriate and gratifying to have as eminent a clay mineralogist as Professor Grim discuss the organization of water on clay mineral surfaces.

● THE OBJECTS of this paper are to gather together the evidence indicating that the water held on the surfaces of clay particles has some sort of definite geometric organization, and to discuss the implications of such water characteristics for some of the properties of clay-water systems.

In clay-water systems containing relatively large percentages of water, such factors as particle charge, shape, etc. may exert a controlling influence on the properties. On the other hand, when the percentage of water is relatively small, as in the case of systems in the plastic state, the thickness of the water film between particles is such that the characteristics of the water itself must play a significant role in determining properties. It is suggested that data obtained by studying highly fluid systems may not be applicable directly to plastic systems, because in the former case, the character of the water would be relatively unimportant, whereas in the latter case it would exert a controlling influence.

EVIDENCE FOR WATER ORIENTATION ON CLAY MINERAL PARTICLE SURFACES

The evidence for some regular orientation of the water particles held on the surface of the clay mineral particles comes from many directions. The characteristics of water molecules themselves, according to the work of Bernal and Fowler (1), Bernal and Megaw (2), and Cross et al. (3), indicate that the water molecules would tend to group into a definite network. In the present symposium the paper by Rodebush and Buswell on the "Properties of Water Substance" shows that the properties of water are such that orientation of water molecules develops at the surface or interface of a solid phase.

Forslind (4) has presented diffraction data which seem to provide direct evidence for orientation in the adsorbed water layers on the clay minerals surfaces. There is urgent need for investigation by neutron diffraction of this matter.

Studies of the properties of clay-water systems provide strong evidence for water

orientation. Grim and Cuthbert (7) have emphasized this point stating that it is extremely difficult to arrive at a satisfactory concept and explanation of such properties without assuming some water orientation. Many examples could be given, but a few will suffice. The heat developed (Heat of Wetting) when clay mineral surfaces are wetted is attributed largely (11) to a change in the nature of the water adsorbed on the surfaces of the clay minerals.

Many cases are known where there is an abrupt change in the physical state of a clay-water system with a slight change in water content. Thus, as increasing amounts of water are added to a dry clay, plasticity develops abruptly; there is a very narrow moisture range in which high bonding strength is developed in a clay-sand system, Figure 1 (7); as water is added to a dry clay, it cannot be extruded until a certain water content is reached when it suddenly becomes easily extrudable, Figure 2. These and many other attributes are easily explained if one con-

siders that the initial water is adsorbed in a rigid oriented state, that as the adsorbed water layers become thick, there is a point at which the orientation is lost or at least greatly reduced in rigidity, and, that the oriented water molecules provide a bonding force between particles.

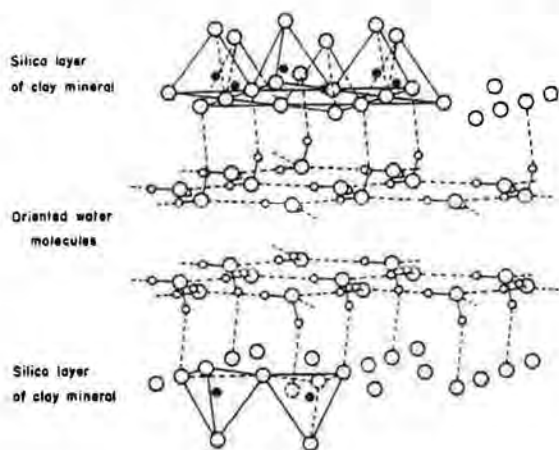


Figure 1. Schematic sketch of orientation of water molecules adsorbed on the basal surfaces of the clay minerals. Large circles represent oxygen atoms; small circles hydrogen atoms; small black or shaded circles silicon atoms (after Hendricks and Jefferson).

WATER ORGANIZATION STRUCTURE

Although students of clays are likely to agree that the water adsorbed on clay mineral surfaces does not have the physical characteristics of liquid water, there is no general agreement on the precise nature of the organization of such water molecules (5). A concept favored by many is that suggested by Hendricks and Jefferson (9) in which successive water layers are composed of water molecules joined into hexagonal groups of an extended hexagonal net. This structure gains credence because of its similarity to the well established structure of water molecules in ice; because of an epitaxial fit with the organization of the oxygen atoms

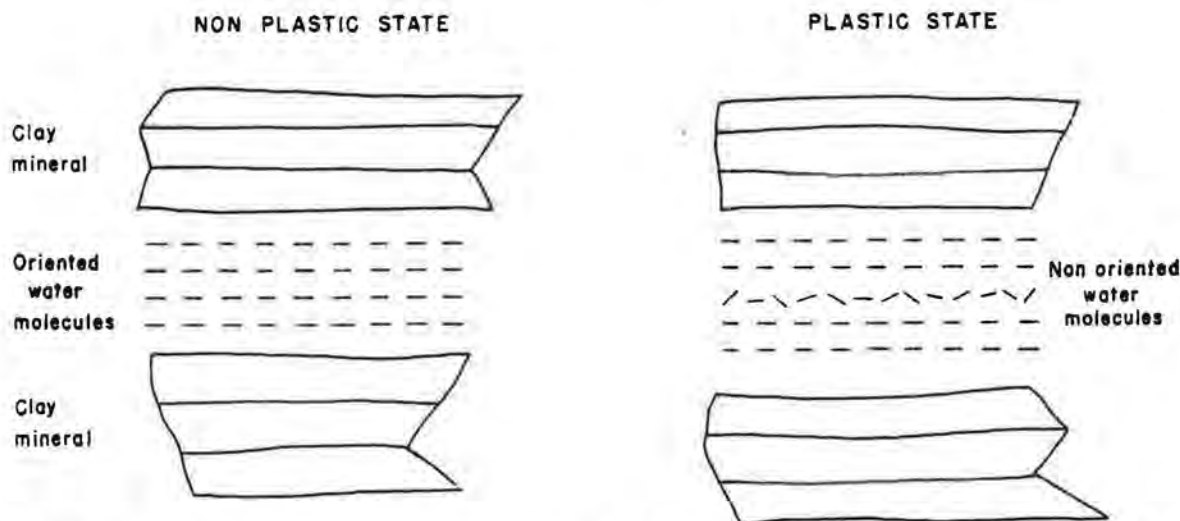


Figure 2. Schematic presentation of character of water in nonplastic and plastic states.

in the basal surfaces of the clay minerals; and because it is in accord with the requirements of hydrogen bonding between the water molecules themselves, successive water layers, and the clay mineral surface.

It seems quite certain, as will be discussed presently, that the water organization is not always exactly the same on all clay particle plane surfaces, and it may well be different on the irregular edges of clay mineral flakes as compared to basal plane surfaces.

The significant point is that the water adsorbed on the clay mineral surfaces and for some distance outward is not in the state of liquid water, but has some organization in which the water molecules are held together by hydrogen bonding.

INFLUENCE OF CLAY MINERAL COMPOSITION

It would be expected that the degree and perhaps kind of water organization would not be the same for all clay minerals, and therefore that the effect of this factor on physical properties would not be the same for all clay mineral compositions. Since the most probable water organization is a sheet structure, flat surfaces would be better than curved surfaces yielded by minerals without cleavage such as quartz, and probably these in turn would be better than the irregular broken edges of the layer-silicate clay minerals.

Some of the flat surfaces of the clay minerals are composed of oxygens, others are made out of hydroxyls. There seems to be no inherent reason why a flat oxygen surface should be better than a flat hydroxyl surface. Perhaps a somewhat different organization of water molecules would develop on the oxygen as compared to the hydroxyl surface. Thus, it might be expected that the structure suggested by Hendricks and Jefferson (9) would favor an oxygen surface because of a preferred epitaxial fit of the water net and the arrangement of oxygens in such clay mineral surfaces.

Another factor in the influence of the clay minerals is the difference in the ease of cleavage into thin flat flakes and/or the ease of penetration of water between the flakes. This factor, of course, determines the amount of flat surface available for water orientation, and it probably would be more important than the kind of surface.

Based on the foregoing considerations, montmorillonite clay minerals would be expected to show the largest amount of oriented water development. Next, but to a considerably smaller degree, would be vermiculite, and weathered degraded illites and chlorites. Next, and also to a considerably reduced degree, would be illites, chlorites and kaolinites, with the micas probably somewhat better than the kaolinites. The halloysite and allophane minerals would be expected to occupy a lower position because their particles may not be flake shaped, although in some cases their extremely small particle size would perhaps outweigh the shape factor.

The exact situation with regard to the fibrous clay minerals, attapulgite-palygorskite-sepiolite, is not certain, but in some cases, at least, their high cleavability and large surface area appears to permit considerable water orientation.

The phenomenon of "Quick" clays, well known to engineers dealing with soils, probably requires the concept of oriented water to provide a satisfactory explanation for their properties (6). Many of these materials are actually silts, and their mineral composition strongly suggests that oriented water can develop on granular particles as well as on the clay mineral surfaces.

INFLUENCE OF ADSORBED IONS

Adsorbed components on the surface of clay particles may serve as a waterproof coating thereby preventing the development of water in a non-liquid state. Common examples would be various types of ionic organic materials. Adsorbed components may also largely control the nature and the extent of oriented water development, and of these inorganic cationic components are probably the most important. Also their influence is best known, and hence, they will be discussed in some detail.

Adsorbed cations influence the development of non-liquid water in several ways as follows: They serve as a bonding force between particles, and thus may determine the available space between particles and the attractive force that growing layers of water

must overcome in pushing apart clay particles. They determine the thickness of the oriented water layers also by the manner in which the cations or the cation plus a hydration envelope can fit into the geometry of the water net. The fit or absence of a fit may serve to enhance or retard the formation of oriented water layers. The cation may determine the actual geometry of the water net, and of very great importance, determine whether the oriented water grades gradually into liquid water or is abruptly separated from liquid water.

In soils and clays the usual adsorbed cations are calcium, magnesium, sodium, potassium, hydrogen, aluminum, and iron.

Calcium, probably the commonest adsorbed cation, in the presence of an abundance of water tends to develop very well oriented water to a thickness of about four molecular layers with any additional water unoriented. There is a sharp break between liquid and non-liquid water. In an air dried state Ca^{++} tends to develop two molecular layers of well oriented water.

In general, and for our purpose, Mg^{++} exerts about the same influence as Ca^{++} . In detail there are some differences: The maximum possible thickness of well oriented water is probably slightly less, and in the air dried state, the geometry of the water is somewhat different so that the thickness of the water layer is slightly reduced.

The sodium ion favors the development of very thick layers (probably tens of molecular layers) if the water is available. Further, the oriented net seems not to be very rigid and there is no abrupt separation between oriented and liquid water. In an air dried state Na^+ favors the development of a single molecular layer, and thus there is a tremendous difference between the thickness of adsorbed water in an air dried state and the potential thickness if moisture is available. Obviously Na^+ clays have very high swelling potential and limit values.

For our purpose K^+ , H^+ , Al^{+++} , and Fe^{+++} may all be grouped together in that they form a tight bond between particles with very small potential for the growth of thick oriented water layers. In an air dried state very thin water layers would be expected. Precise data for some of these cations is difficult to obtain. For example, a prepared hydrogen clay contains Al^{+++} and possibly Fe^{+++} , and the preparation of a K^+ clay is likely to be accompanied by structural changes within the clay mineral itself.

Untreated clays or soils may contain a dominant single adsorbed cation or a mixture of cations. If there is a single cation present, a very uniform oriented water thickness may develop throughout the material which will cause considerable stability. If there is a mixture of cations, there may be variable water thicknesses which would favor instability. In Wyoming bentonites, it has been shown (13) that an adsorbed cation composition of about 70 percent Na^+ and 30 percent Ca^{++} produces the maximum potential dispersibility. Of importance is the point suggested by available data, that the gradual replacement of one cation by another may have no influence on adsorbed water development up to a certain point at which there is a sudden abrupt change in the stable thickness of the oriented water.

This factor of the abruptness of transition of water from one state to another is probably related to the distribution of cations on the clay mineral surfaces. It has been shown recently that in some clays containing both Ca^{++} and Na^+ , the Ca^{++} are concentrated on some surfaces, and the Na^+ on others rather than having a random scattering of Ca^{++} and Na^+ on all surfaces. Since the population of any surface by Ca^{++} or Na^+ is probably never completely monoionic, it is logical that there could be a certain amount of exchange without influencing the adsorbed water layer stability. This is probably a factor in determining abruptness characteristics of changes in water orientation. It must be remembered that there is much yet to be learned regarding the relation of the distribution of cations within a clay or soil to adsorbed water characteristics.

Recently Slovinsky (12) has shown by means of continuous X-ray diffraction analyses that the loss of adsorbed water by montmorillonite clays takes place in a stepwise fashion rather than continuously. Thus, there is the loss of one molecular layer, then a second layer, and so on. This seems to be the case regardless of which of the common adsorbed cations are present. Such a stepwise dehydration must be accompanied by a stepwise abrupt change in volume and bonding strength between particles.

IMPLICATIONS OF ORIENTED WATER STRUCTURES

Oriented water molecules on clay particle surfaces undoubtedly act as a bonding force between the particles. Liquid water would be expected to produce comparatively little bonding strength. This difference in bonding strength is the essential factor regarding the state of the adsorbed water so far as the physical properties of clay - water systems are concerned. To this generality must be added the point that adsorbed ions and molecules on the surfaces of clay particles act directly by influencing the bonding force between the particles, and indirectly by influencing the organization of the water molecules and thereby its bonding force.

On the basis of the foregoing considerations the following statements seem warranted:

There could be materials with very high moisture contents which would have considerable strength. Such materials are likely to be composed largely of montmorillonite and carry sodium as the exchangeable cation. Soil materials and clays composed of attapulgite or very poorly organized clay minerals might also have these properties.

A material can exhibit tremendous difference in strength with a slight change in moisture content. If a material is holding about its maximum amount of rigid water, additional water would be in the liquid state with the likelihood that the water bond between the particles would be broken. Also, the loss of a slight amount of moisture by drying might well disrupt an equilibrium thickness of water layer so that strength would be destroyed.

A slight change in the adsorbed cation composition might well cause a destruction of the orientation of some water molecules because the replacing cation would not permit the same maximum amount of oriented water as the replaced cation. In the case of the replacement of Na^+ by Ca^{++} or H^+ the permissible oriented water thickness would be reduced—this might develop liquid water and immediate loss of strength, or the oriented water might continue to exist but in an unstable form which later would be changed to liquid water by the addition of more water, or perhaps by the application of some external abrupt shock force which would suddenly break the water net. In the case of an exchange of Na^+ for hydrogen or a multivalent cation, the maximum oriented water holding capacity would be increased, but the perfection of orientation and hence the bonding strength of the water net would be reduced. As a consequence of replacement with Na^+ , one would expect, therefore, a more gradual loss of strength, and of course, if additional moisture were available, an expansion in volume or swelling of the clay.

As just noted above, there would be clays and soils where volume would increase with increased moisture control. Such expansion would be accompanied probably at first with only a slight decrease in strength and later with a substantial gradual decrease of strength. The gradual decrease is a consequence of the great thicknesses of oriented water layers possible when Na^+ is the adsorbed cation, and the gradual decrease in the degree of rigidity of the oriented water layers outward from the adsorbing surface. Montmorillonite would be the clay mineral component expected in swelling clays since it permits water to enter between the individual unit silicate cell layers, i. e. the swelling takes place within the silicate structure. Some swelling within the silicate particles might also develop in some poorly organized clay minerals. In clays composed of other clay materials the water is in pores and around large crystal units and particles so that the development of oriented water would not be expected to cause a substantial increase in volume, i. e. the expansion under ordinary conditions would be insignificant.

It follows from considerations of rigid water, that soils and clays can experience a reduction in volume, aside from any association with surface drying and without the application of an external force. This can occur following the liquification of adsorbed water if the setting is such that the liquid water may be removed, as by seepage downward into the ground water. Conceivably, such a reduction in volume could also occur without the removal of any water. Thus, there may be material with a water bond in which there are pores not completely filled with water. Also, if the structure suggested by Hendricks and Jefferson (9) is the correct one, the oriented water could have a density less than liquid water so that there would be a reduction in volume when the water structure was lost.

A consequence of the development of oriented water, which is somewhat unexpected, is the existence of a time factor in the development of the properties of clay-water systems. Thus it has been observed (7) that the compression strength of some moist clay-sand systems increases during a matter of hours after mixing and compacting into a test piece without any change in the moisture content. This is readily understandable on the basis that some time is necessary for the moisture to penetrate the clay mass to all potential surfaces and for the water structures to develop. The development of oriented water is a kind of crystal growth and, as is common in crystal growth, requires time. One would expect that the time factor would be particularly important in materials composed of mixed-layers, degraded illites and chlorites, and perhaps halloysites. Under certain conditions attapulgite clays should also show this phenomenon but for a somewhat different reason, since the bundles of elongate particles of this mineral are cleavable, but with some difficulty. As an attapulgite-water system is worked or agitated, the mineral particles are separated by cleavage thereby increasing the surface area for water adsorption. This same growth of surface by cleavage of particles takes place in all the clay minerals, but probably not to the extent or with as great an influence on clay-water properties as in the case of materials composed of attapulgite.

Materials whose properties would be most influenced by oriented water considerations would be likely to be those with high limits and high sensitivity. However, some materials of low activity, for example, some silts with a low clay mineral content, are also thought to have oriented water bonds which are responsible for their high sensitivity. In such materials the detailed factors of composition, both textural and mineral, which favor the development of the high sensitivity are not well understood. Rosenquist (10) has shown that an exchange of cations, as by leaching of Na^+ plays a role, but it seems doubtful if all very sensitive silts have been subject to such leaching action.

It seems obvious from the foregoing discussion that an engineer needs to give particular attention to the moisture content of soils and clay materials with which he is required to deal, and to any potential cation exchange which might change the nature and the extent of the adsorbed water. Conceivably it might be desirable to go to great lengths to maintain the moisture content and to prevent an exchange reaction in order to insure that the water orientation and attendant strength would not change abruptly. Thus, drainage favoring a variable change in the adsorbed moisture content might not stabilize the slope but be disastrous because it might tend to alter the nature of the adsorbed cation and the strength of the water bond.

REFERENCES

1. Bernal, J. D., and Fowler, A. H., "A Theory of Water and Ionic Solution with Particular Reference to Hydroxyl Ions." *J. Chem. Phys.* 1, 515-548 (1933).
2. Bernal, J. D., and Megaw, H. D., "The Function of Hydrogen in Intermolecular Forces." *Proc. Roy. Soc. (London) A*, 151, 384-420 (1935).
3. Cross, P. C., Burnham, P., and Leighton, P. A., "The Raman Spectrum and the Structure of Water." *J. Am. Chem. Soc.* 59, 1134-1147 (1937).
4. Forslind, E., "The Crystal Structure and Water Absorption of the Clay Minerals." *Trans. 1st Intern. Ceram. Congr.* 98-110 (1948).
5. Grim, R. E., "Clay Mineralogy." McGraw-Hill, 384 pp. (1953).
6. Grim, R. E., "The Composition in Relation to the Properties of Certain Soils." *Geotechnique* 1, 139-147 (1949).
7. Grim, R. E., and Cuthbert, F. L., "Some Clay-Water Properties of Certain Clay Minerals." *J. Am. Ceram. Soc.* 28, 90-95 (1945).
8. Grim, R. E., and Cuthbert, F. L., "The Bonding Action of Clays: Pt. 1, Clays in Green Molding Sands." *Rept. of Inv. 102, Ill. Geol. Survey*, 36 pp. (1945).
9. Hendricks, S. B., and Jefferson, M. E., "Structure of Kaolin and Talc-Pyrophyllite Hydrates and Their Bearing on Water Sorption of Clays." *Am. Mineral* 23, 863-875 (1938).
10. Rosenquist, T., "Sensitivity of Norwegian Quick Clays." *Geotechnique* 3, 195-200 (1953).

11. Siefert, A. C., "Studies on the Hydration of Clays." Ph. D. thesis, Pennsylvania State University (1942).
12. Slovinsky, R. L., "Mineralogical Variation of Wyoming Bentonites and Its Significance." Ph. D. thesis, University of Illinois (1958).
13. Williams, F. J., Neznayko, M., and Weintritt, D. J., "The Effect of Exchangeable Bases on the Colloidal Properties of Bentonite." J. Phys. Chem. 57, 6-10 (1953).