The Importance of Pore Water Chemistry on Mechanical and Engineering Properties of Clay Soils

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The importance of pore water chemistry on mechanical and engineering properties of clay soils

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The classical Coulomb–Terzaghi shear strength equation, $s = c + (\sigma - u) \tan \phi$, depends not only upon mechanical and mineralogical factors, but to a high degree upon the total chemistry of the system. Changes in chemistry owing to natural and anthropogenic factors may change the strength properties of a given clay soil at a given water content. The classical example of slow acting chemical changes is the development of quick clay properties. Modern infiltration of different electrolytes and detergents from leaking sewer systems may change shear strength and compressibility of the ground. These processes are different in clays of expanding and non-expanding minerals. The importance of the different cation species seems to depend upon valency and polarizability. Influence of anions is more complicated and depends upon interaction with edge charges and the crystalline properties of the clay minerals.

As we know clay does not represent any definite chemical or mineralogical compound and may vary considerably even within a limited geographical area. Different clays may have very different mechanical properties. The reason for calling similar types of geological material 'clay' in different languages seems to have been that they have some mechanical properties in common. These may be plasticity, thixotropy, etc., depending upon mineral/water ratios. However, these properties are dependent upon many factors.

Until X-ray studies, combined with various other methods of micromineralogy, made it clear how the mineral phases varied from clay to clay, there was little accurate idea of their nature. The shear strength properties of all soils have, however, some features in common. These had been recognized by Coulomb in 1776, when he introduced the shear strength equation:

$$s = c + \sigma \tan \phi. \tag{1}$$

This states that the total shear resistance of a soil (s) can be considered as the sum of cohesive resistance (c) and the frictional term, σ, being the normal stress upon the surface of slippage and ϕ the angle of internal friction.

Von Terzaghi (1925) established the fundamental basis for soil mechanics. He introduced the concept of *effective stresses*, showing that the total stresses of Coulomb gave misleading results. Terzaghi's equation may be given as follows:

$$s = c + (\sigma - \bar{u}) \tan \phi, \tag{2}$$

$\bar{u}$ being the pore water pressure, i.e. the pressure in the voids in the soil. $(\sigma - u)$ may be written as $\bar{\sigma}$, the effective stress on the shear plane. The next major step forward was taken by Hvorslev (1937). He confirmed in principle the law of Coulomb–Terzaghi, but for any given clay, cohesion was found to be a function of water content. He therefore extended Coulomb's equation:

$$s = \bar{c} + \bar{\sigma} \tan \phi \tag{3}$$

in which $\bar{c}$ now depends on the water content whereas c in (1) may be independent of water content. This dependence can be expressed by the introduction of the *equivalent* consolidation pressure θ_c, with a constant H:

$$s = H\sigma_c + \bar{\sigma} \tan \phi. \tag{4}$$

The significance of the result of Hvorslev's investigations is very profound. The two main results: dependency of the cohesion on water content with a given mineralogy and chemistry, and recognition of the angle of internal friction as a soil characteristic which determines the strength of even rather plastic and fine-grained clays were most important steps in the advancement of knowledge of the fundamental strength properties of soils.

Hvorslev's investigation was carried out on remoulded soils, and his results are valid only for such material. This has often been forgotten by many research workers dealing with clay soil properties. As seen from an electron micrograph of *normally consolidated clays*, these consist of aggregates of platy minerals touching each other by corner-to-plane contacts in more or less dense cardhouse structures. Any deformation of such a body will necessarily involve a mutual movement of the particles relative to each other and a corresponding flow of the water in interstitial voids. As chemical electrostatic forces will act between the individual minerals at the points of contact, the deformation process must necessarily be complex; indeed it may *be stated that the strength of clay materials is not fully understood.*

Terzaghi's concept of effective stresses is still fully valid. If we consider a soil sample, we conclude from a general mathematical principle on invariance that any scientifically correct failure criterion must include the three effective principal stresses σ_1, σ_2 and σ_3. Several attempts have been made to solve the general failure problem, but because of lack of experimental data and insufficient theoretical understanding, we are unable to treat the complete problem, even for isotropic soils, especially as these become anisotropic as a result of deformation. By using originally anisotropic bodies with changing anisotropy, a complete solution of the frictional term has been attempted, but in vain. That cohesion is a function of the stress history and not only of the actual set of stresses adds to the complexity of the problem.

In practice, however, it has been proved that σ_1 and σ_3 are of the greatest importance for the strength, and engineering practice is to work with failure criteria where only these two principal stresses are used. In most cases we choose to put $\sigma_2 = \sigma_3$. This is done in all tests of the triaxial compression type. Thus we ignore the influence of the intermediate principal stress σ_2.

According to the Hvorslev concept of failure, a clay body exposed to a stress ellipsoid with rotational symmetry will have a plane of failure with the angle $45° + \frac{1}{2}\phi_r$, where the subscript r is used to emphasize the rotational symmetry to the σ_3 direction. As shown above, the Hvorslev true or real conditions of failure are based upon effective stresses in a given soil material having a constant voids ratio (ratio of pore volume to solids volume) under variable external conditions. If, on the other hand, the voids ratio varies as a function of external stresses, we may determine a set of Mohr circles for the effective stresses at failure. In this way, the envelope curve will determine the effective failure conditions, and we obtain the values for c and ϕ called respectively *effective cohesion* and *effective angle of friction.*

To determine c_r, ϕ_r, $\bar{c}$ and $\bar{\phi}$, respectively, we have to know the pore water pressure at failure.

In certain cases it is possible to analyse the problem of failure approximately only by total stresses. This gives us c and ϕ at Coulomb's conditions of failure called *the apparent cohesion* and *the apparent angle of friction*.

Several hypotheses have been advanced as to the nature of cohesion and friction in clay soils. The fact that clays are colloidal materials indicates that electrochemical forces are involved, at least in the cohesional terms (see below), probably also in the frictional term.

As all the failure equations from Coulomb to Hvorslev deal only with the bulk properties, that is, the macroscopic stress ellipsoid and the pore water pressure, it is obvious that none of these equations can predict the attractive and repulsive forces acting between the charged mineral particles, nor do they evaluate the cementing action of precipitated mineral substances at all the points and areas of contact between the minerals. This stresses the importance of the title of Hvorslev's (1937) paper. His equation was given for completely remoulded material where any cementing action could be ignored. In all natural geological deposits, we have to assume that secondary cementation may exist.

Among other authors, Denisov & Reltov (1961) have demonstrated the influence of natural cementing bonds. Such a cementation may be included as a *nonreversible* cohesion term, whereas some of the electrochemical forces may be included in the stress conditions as a set of internal stresses adding to the set of external effective stresses. The latter especially, will depend upon chemical changes in the pore water and mineralogical changes of the minerals. Thus for example, the subpolar *quick clays* have obtained their peculiar properties from secondary chemical changes in flocculated and slightly overconsolidated clays, these chemical changes being of a nature which increased the zeta potential of the minerals. This was dealt with by Rosenqvist (1977).

The simplest chemical change is represented by the leaching of salt from marine deposits owing to the seepage of rain water. Another reaction which will cause a similar effect upon the zeta potential is represented by the action of organic complexing anions from decaying humus. In both cases, soils of high sensitivity may develop. By *sensitivity* we understand a permanent loss of strength by remoulding, observed in many clays. If a clay sample of a given natural strength is thoroughly remoulded and the strength immediately measured, we mostly observe a considerable drop in the shear strength value. By storage, the strength gradually increases, but in many soils, it will never arrive at the initial values unless the water content drops, either by desiccation or by syneresis. Such a stored clay will again by a subsequent remodelling arrive at the same low shear strength as the original sample. Thus there is a reversible loss of strength in remoulded samples (thixotropy) and a nonreversible loss of strength in natural soils. This loss of strength is called sensitivity, and the ratio between the initial strength and the remoulded values is called *sensitivity value*. In the typical quick clays, the sensitivity may have values of more than 100, whereas the thixotropy value may only be 2–5. Thus these clays will lose 99% of the initial strength by remoulding, and only 2–5% of the initial strength will be regained by storage.

These processes seem to be restricted to clays of non-swelling minerals (illites, chlorites, kaolinite). In soils of some swelling minerals such as smectites, the chemical changes that cause the high sensitivity of quick clays may cause a *decrease* in the sensitivity. This is probably due to the volume change of the mineral phase caused by swelling. In such cases we may find that changes that reduce the sensitivity value of illitic clays may increase the sensitivity value of smectitic sediments.

Ever since the early days of modern soil mechanics, much emphasis has been given to the problem of the water in clay soils. Only recently, modern techniques, using diffusion of isotope tracers combined with nuclear magnetic resonance and infra red spectroscopy, have shown that the greater part of the aqueous phase of clay soils has *properties that are not fundamentally different* from those of water. However, through a transition zone of more or less gradually increasing rigidity, this free water in the voids becomes firmly bound water molecules on the surface of the clay minerals. Thermodynamically, and probably also mechanically, these innermost *one to three* water layers seem to have properties like those of a solid body. As any failure in a clay sediment involves a shearing in this innermost water, it is necessary to have a better knowledge of the innermost water in order to understand the physical basis for any rheological model of clay.

Johnson (1970) developed a rheological model describing the flow behaviour of remoulded clay material at a finite rate of deformation. This model is called a *Coulomb-viscous model*. It has the form:

$$\tau = c + \sigma_{\mathrm{n}} \tan \phi + \eta, \frac{\mathrm{d}\epsilon}{\mathrm{d}t}, \quad \text{i.e.,}\ \tau > c + \sigma_{\mathrm{n}} \tan \bar{\phi}, \tag{5}$$

where τ is internal shear stress, σ_{n} is internal normal stress, ϕ is the angle of internal friction, η is viscosity, and ϵ is rate of shear strain (velocity gradient). In this case, it has to be noted that the cohesional term is not identical to the cohesion at rest.

We observe in all clay water systems a certain relaxation time if the strain rate is changed. If the strain rate is decreasing, we first observe a decreasing resistance against deformation, and after some time, a slow return to the constant value. On the other hand, if suddenly the rate of deformation is increased, we observe a temporary increase in resistance against deformation, and then a slow return to normal value.

It seems that an explanation of such data needs a rheological model differing from most ‘spring and dashpot models’ previously presented. In most cases these do not satisfy the observed consolidation curves either. We may consider two clay mineral particles under undisturbed conditions. We assume that they more or less touch each other at a point or a small volume of contact, and we assume that surrounding that area we have a small volume of coherently organized oxygen and hydrogen. The material in this volume behaves more or less like a solid substance of a given breaking strength. When the shear stress in the contact area exceeds a certain limit, the coherent structure will be broken, and the resistance F against mutual displacement will decrease with increasing rate of strain, that is, in accordance with the formula

$$F = a \Big/ \left(1 + \frac{\mathrm{d}\epsilon}{\mathrm{d}t}\right), \tag{6}$$

where a is a constant. The material thus shows *negative strain hardening*. This is characteristic of crystals where a limited number of dislocations arise by strain, and where the dislocations may diffuse out of the structure after rest.

The influence of exchangeable cations upon the shear strength of a remoulded clay depends very much upon the type of minerals in the fine fraction. In systems of non-swelling clay minerals, such as illitic-chloritic clays in Scandinavia and Canada, we found that not only the liquid limit but also the shear strength of the same clay mineral, having the various alkali ions in the water phase, regularly increases in the series $\mathrm{Li^+}$, $\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Cs^+}$ at any given water content.

The positive cations are expected to be present on the basal planes of the clay mineral flakes, and to be absent from the edges and corners of the flakes. It may therefore be suggested that the van der Waals attraction in corner-to-plane contact is a function of the first power and not of the second power of the polarizability of the counter ion.

It we have a system with remoulded expanding clay minerals belonging to the smectite group, we have a different relationship. In these cases the shear strength seems to increase through the series K^+, Rb^+ and Cs^+, but decreases from Li^+ and Na^+ to K^+, at the same water content. Thus, at any given water content a K^+ smectite clay is softer than an Na^+ smectite clay at the same water content. This may result from the prevention of lattice expansion by the larger alkali cations, whereas the lithium and sodium clays are much more expandable, which is well known and will not be dealt with further in this paper.

The action of anions upon the shear strength is much more complicated. The dispersing action of polymetaphosphates and several organic humic anions has been qualitatively discussed several times, but quantitative data are rare. The use of equivalent concentrations of sodium salts of fluorine, chlorine, bromine, iodine, chromate and sulphate give different values for viscosity of clay water semi-liquids. Wendelbo (1983) has described the influence of these ions upon clay material, in which he believed he had blocked the edge charges by polymetaphosphate, and it seems that these comparatively small anions have a moderate influence upon the basal charge of the clay minerals.

The data for *critical coagulation concentration* in diluted suspensions of kaolinite and smectite show the mutual influence of some simple anions and polymetaphosphates upon the attractive and repulsive forces between the minerals. The Bingham yield value of more concentrated clay water suspensions follow similar relations for the simple anions, in the case of smectites and kaolinites.

In the case of gibbsite–water systems at pH values where the minerals are positively charged the c.e.c. depends to a marked degree upon the charge of the anions in the order $PO_4^{3-} < SO_4^{2-} < Cl^-$. These data indicate that there is negligible adsorption or ion pair formation of the investigated anions upon the basal surface of the layered silicates, and the influence of these relatively small ions upon the charge properties of clays is probably due to adsorption upon *the broken edges*. The softening of clays at constant water content by addition of phosphate and silicate ions from detergents may be explained at least qualitatively in this way.

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