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Physico-chemical state variables for clay soils
Variables d'état physico-chimiques des sols argileux

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SYNOPSIS: The classic principle of effective stress does not provide a complete description of the stress state that controls volume change or shear strength of a clay if a change in pore fluid chemistry is involved. In this paper, a more complete set of stress state variables are developed using a multiphase continuum mechanics approach. It is shown that for saturated soils two stress state variables are required to describe the stress state. These include the classic effective stress and a physico-chemical stress state variable which represents the net electrostatic repulsive stresses between the soil particles. Laboratory test results are used to illustrate a three-dimensional constitutive surface for volume change that is described by a relationship between void ratio, effective stress, and the physico-chemical stress state variable.

1 INTRODUCTION

The development of the principle of effective stress by Terzaghi (1936) heralded the beginning of theoretical soil mechanics. This principle stated that changes in the volume or shear strength of a soil occur as the result of changes in the effective stress, that is, the difference between the total stress, σ, and the pore-water pressure, u_w. This principle is consistent with, and can be shown to be based on continuum mechanics. In this approach the "state" and "stress state" of a soil system is defined for a Representative Elementary Volume (REV) of the continuum as follows (Fredlund 1987):
 (1) State: non material variables required for the characterization of a system.
 (2) Stress state variable: the variables required for the characterization of the stress condition.
Changes in the stress state of the system can be linked to the deformation and the shear strength of the system through constitutive relationships which contain material properties. It follows that the effective stress principle can be extended to assert that no change in behavior will occur unless there is a change in the stress state variable.

When clay soils are subject to changes in pore fluid chemistry a difficulty arises with the use of the classic effective stress state variable for saturated soils (i.e., $\sigma - u_w$).

Although there may be no changes in the total stress or pore fluid pressure in a specimen, changes in the strength, volume change, and permeability have been observed (Bolt 1956, Mesri and Olson 1971, Dunn and Mitchell 1984, Kenney 1967). In practice, these changes in soil behavior have usually been incorporated into the soil properties by ensuring that tests conducted in the laboratory duplicate the pore fluid chemistry present in the field. This approach, however, cannot account for transient changes in soil behavior during changes in pore fluid chemistry and may not prove to be the best approach for geotechnical practice. In modern geotechnique more and more engineers are being faced with design of waste containment systems in which the natural and compacted soils routinely experience wide variations in pore fluid chemistry over their design life. Consequently, a more general approach is needed to allow changes in the "chemical" stress state to be incorporated into conventional analyses.

2 DIFFUSE DOUBLE LAYER THEORY

Most clay minerals have a net negative surface charge. In order to obtain electroneutrality, a diffuse double layer of cations and anions develops around the clay particle. The negatively charged clay surface and the charge distribution adjacent to the clay particle is termed the diffuse double layer. Theoretical descriptions of the diffuse double layer were first proposed by Gouy (1910) and Chapman (1913) and later modified by Stern (1924).

Mitchell (1976) has shown that the distance to the center of charge density surrounding a semi-infinite negatively charged clay particle, that is, the "thickness" of the double layer, changes in response to changes in pore fluid chemistry such as concentration, cation valence, and dielectric constant.

3 INTERPARTICLE STRESSES

Changes in the volume or shear strength of soil occur in response to changes in stresses transmitted directly between particle contacts. These interparticle stresses include; long range stresses due to electrostatic repulsion (i.e., stresses resulting from diffuse double layer effects) and van der Waals stresses, and short range stresses that result from Born repulsion and surface hydration or primary valence and cementation bonds. In most clays the dominant long range stress between particles is electrostatic repulsion (Bailey 1965, Mitchell 1976).

Numerous attempts have been made to predict the net repulsive stress, (R-A), for pure clay

systems using the assumption that all interparticle stresses are transmitted by the electrostatic stresses. The conceptual model applied in these calculations is called the osmotic pressure concept. The clay system is assumed to exist as a series of perfectly dispersed, parallel, clay particles. The equation describing the charge density distribution and electric potential around a single particle can be integrated to obtain the mid-plane electrolyte concentration and the potential half way between the clay particles. The overlapping diffuse layers are considered to behave as semi-permeable osmotic membranes. The difference in osmotic pressure between the bulk pore fluid and the fluid between the clay particles is then taken to be equivalent to the net repulsive stresses between the particles. Detailed developments of the osmotic pressure concept are provided by Bolt (1956) and Mitchell (1976).

During the 1950's and 1960's a number of researchers attempted to use the osmotic pressure concept to predict the compressibility of pure clays under varying pore fluid concentrations (Bolt 1956, Bolt and Miller 1955, Warkentin et al 1957, Aylmore and Quirk 1962, Blackmore and Miller 1962, Warkentin and Schofield 1962, Mesri and Olson 1971). The result of these studies, however, was that with the exception of pure homoionic clays at high void ratios, the osmotic pressure concept only provided a qualitative description of soil compressibility. The major limitations with this technique were that the assumptions of a perfectly dispersed particle arrangement and the dominance of the electrostatic stress between particles were not generally satisfied.

4 "TRUE EFFECTIVE STRESS"

The work described above dealt with the physico-chemical stresses at a microscopic level rather than the macroscopic level used in the definition of classic effective stress for a saturated soil. During the 1960's and 1970's several researchers, including Lambe (1960), Balasubramonian (1972) and Chattapadhyay (1972), attempted to extend the effective stress equation to include the net long range electrostatic stress as follows:

$$\sigma^* = (\sigma - u_w) - (R-A) \qquad [1]$$

where:
σ^* = "true" effective stress
σ = total stress
u_w = pore water pressure

(R-A) = net long range electrostatic stress

This "true effective stress" was developed from an analyses of static equilibrium of normal forces perpendicular to a wavey plane passing between soil particles. Although it provides a statement of the equivalence of stress, it is not based on an appropriate free body diagram and consequently is not an appropriate means of developing stress state variables (Fredlund, 1987).

To be an appropriate stress state variable, the components of the stress state must be shown to be equally effective in controlling soil behavior. Fredlund and Morgenstern (1977) demonstrated this concept for stress states for unsaturated soil through the use of null tests. Similar tests for "true" effective stress were

conducted by Balasubramonian (1972) on clay shales. Morgenstern and Balasubramonian (1980) demonstrated that during leaching of a dense clay shale, changes in the predicted (R-A) stress were balanced by changes in the total stress required to maintain a constant specimen volume. It is important to note that the shale used was predominately montmorillonitic and consequently the assumption regarding the dominance of electrostatic repulsion is likely valid. This would not be true for clay soils in general.

5 PHYSICO-CHEMICAL STRESS STATE FROM CONTINUUM MECHANICS

In the continuum mechanics of multiphase mixtures the behavior of each phase is dictated by the stresses acting on that phase. Fredlund (1973) states that the first two steps in this approach are the description of the physical multiphase element or Representative Elementary Volume (REV), and the establishment of the state variables associated with each phase.

5.1 Representative Elementary Volume (REV)

An element of saturated soil can be considered as a three phase system consisting of the soil particles, the pore fluid, and the diffuse double layer or adsorbed fluid hull surrounding each soil particle (Fig. 1). The diffuse double layer includes the surface charge along the clay particles. By definition, a phase must possess differing properties from the contiguous homogeneous phases and must have a continuous bounding surface throughout the element. The unique properties of the diffuse double layer have been documented by Mitchell (1976). The existence of a distinct boundary surface is not as well defined but the extent of the adsorbed fluid phase is described by double layer theory.

The porosities of each phase of the elementary volume may be defined as follows:

n_p = volume of soil particles / total elemental volume

n_f = volume of bulk pore fluid / total elemental volume

n_d = volume of diffuse double layer / total elemental volume

The sum of the phase porosities is equal to unity.

5.2 Equilibrium equations for each phase

The principle of superposition of coincident equilibrium stress fields may be used as described in continuum mechanics (Truesdell, 1966). The assumption is made that an independent continuous stress field is associated with each phase of the multiphase system. The number of independent force equilibrium equations that can be written is equal to the number of cartesian coordinate directions multiplied by the number of phases constituting the continuum (Fredlund 1987).

Force equilibrium for the element is ensured by independently considering equilibrium for each phase. The elemental forces consist of surface tractions, gravity body forces and interaction forces between the phases. The interaction body forces between the phases are as follows:
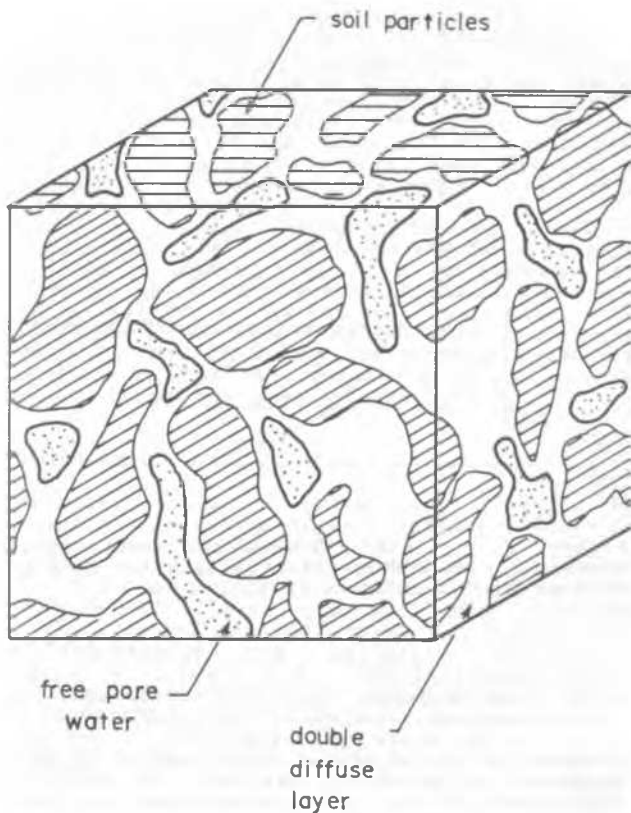
Figure 1. Element of saturated soil illustrating the diffuse double layer

F_f = interaction force between the diffuse double layer and pore fluid

F_d = interaction force between the soil particles and the diffuse double layer

Equilibrium stress systems acting on the overall element and the diffuse double layer and bulk pore fluid phases are considered.

We can assume that the electrostatic interactions between particles can be described by the net repulsive minus attractive stress (R-A) acting within the diffuse double layer. This is conceptually similar to the osmotic pressure concept, in which the repulsive stress is equated to the osmotic pressure difference within the pore fluid. A second assumption is that when (R-A) is expressed as a stress tensor it is isotropic and does not contain shear stresses. The density of the diffuse double layer is assumed to be equal to the density of the pore fluid.

Equilibrium equations can be written for the overall soil element as well as for each phase. A one-dimensional form of the equilibrium equations in the y-direction can be written as follows:

Overall Element:

$$\left(\frac{\partial \tau_{xy}}{\partial y} + \frac{\partial \sigma_y}{\partial y} + \frac{\partial \tau_{zy}}{\partial y} + \rho_t g\right) dx\ dy\ dz = 0 \quad [2]$$

Pore Fluid:

$$\left(n_f \frac{\partial u_f}{\partial y} - F_f + n_f \rho_f g\right) dx\ dy\ dz = 0 \quad [3]$$

Diffuse Double Layer:

$$\left(n_d \frac{\partial (R-A)}{\partial y} - F_d - F_f + n_d \rho_f g\right) dx\ dy\ dz = 0 \quad [4]$$

where:

σ_y = normal stress in the y-direction

τ_{xy} = shear stress on the x-plane in the y-direction

τ_{zy} = shear stress on the z-plane in the y-direction

u_f = pore fluid pressure

ρ_t = total density of the soil

ρ_f = fluid density

Equations [2] through [4] are statements of equilibrium for the overall element, the pore fluid, and the double layer. Volume change of the soil structure is controlled by the interparticle interactions between the soil particles. However these interactions cannot be measured directly. An equation for the stresses effective at the interparticle contacts can be written as the difference between the statement of equilibrium for the entire element, and those for the pore fluid and double layer phases. This equation is then written as follows:

$$\frac{\partial \tau_{xy}}{\partial y} + \frac{\partial \sigma_y}{\partial y} + \frac{\partial \tau_{zy}}{\partial y} + \rho_t g - n_f \frac{\partial u_f}{\partial y} - n_d \frac{\partial (R-A)}{\partial y} +$$

$$2F_f + F_d - \rho_f g\ (n_d + n_f) = 0 \quad [5]$$

By adding and subtracting $n_d\ (\partial u_f / \partial y)$ and $n_f\ \partial(R-A)/\partial y$ and combining terms, the following equilibrium equation for the soil particles can be obtained:

$$\frac{\partial \tau_{xy}}{\partial y} + \frac{\partial(\sigma_y - u_f - (R-A))}{\partial y} + \frac{\partial \tau_{zy}}{\partial y} + \rho_t g +$$

$$(1 - n_f)\frac{\partial u_f}{\partial y} + (1 - n_d)\frac{\partial(R-A)}{\partial y} + 2F_f + F_d -$$

$$(n_f + n_d)\ \rho_f g = 0 \quad [6]$$

An examination of this equation reveals the presence of three sets of surface tractions (i.e., $(\sigma_y - u_f - (R-A))$, u_f, $(R-A)$). In a similar development for the stress state variables for unsaturated soils Fredlund and Morgenstern (1977) suggested that the (u_f) term

can be eliminated if the assumption is made that the soil particles are incompressible. If the diffuse double layers in the soil are extensive and completely overlapping then a similar assumption for the (R-A) term would also be valid. The remaining stress state variable is identical to that of true effective stress (i.e., $(\sigma_y - u_f - (R-A))$). The test results of Morgenstern and Balasubramonian (1980) provide verification for this combination of stresses as a single stress state variable for the case of a montmorillonitic clay shale.

In a more general case, it is likely that the diffuse double layers will not be extensive and consequently two stress state variables remain (i.e., $(\sigma_y - u_f - (R-A))$ and $(R-A)$). It is not appropriate to include $(R-A)$ in both stress state variables. If only the term $(n_d \, \partial u_f / \partial y)$ is added and subtracted from Equation [5] the resulting equilibrium equation is as follows:

$$\frac{\partial \tau_{xy}}{\partial y} + \frac{\partial (\sigma_y - u_f)}{\partial y} + \frac{\partial \tau_{zy}}{\partial y} + \rho_t g + (1 - n_f) \frac{\partial u_f}{\partial y} -$$

$$n_d \frac{\partial (R-A)}{\partial y} - (n_f + n_d) \rho_f g + 2F_f + F_d = 0 \quad [7]$$

From this equation two stress state variables emerge (i.e., $(\sigma_y - u_f)$ and $(R-A)$) if the u_f term is again eliminated as before. Two stress state variables then control soil behavior; the effective stress, $(\sigma - u_f)$, and the physico-chemical stress represented by $(R-A)$. This is similar in form to the stress state variables for unsaturated soil (i.e., $(\sigma_y - u_a)$ and $(u_a - u_w)$) proposed by Fredlund and Morgenstern (1977). Fredlund and Morgenstern (1976) used a three-dimensional constitutive surface for volume change to relate changes in void ratio to changes in matric suction and net total stress. A similar constitutive surface for the physico-chemical stress state variables drawn from the compressibility data of Mesri and Olson (1971) is illustrated in Figure 2. Two variables are essential because changes in matric suction are not as "efficient" in producing changes in volume change and shear strength as are changes in total stress. This has also been shown to be true for $(R-A)$ and $(\sigma_y - u_f)$. As illustrated in Figure 2 each stress state variable is linked to volume change through a separate modulus. Laboratory testing to obtain the osmotic compressibility modulus for two clay soils (Regina Clay and a Sand/Na montmorillonite mixture) was conducted by Barbour (1987a) and reported by Barbour (1987b) and Barbour and Fredlund (1988).

5.3 Practical physico-chemical stress state variables

A difficulty remains in the practicality of the physico-chemical stress state variables. Fredlund (1987) suggested that the choice of an appropriate set of stress state variables has to also consider whether:

(1) the variables can be experimentally tested,
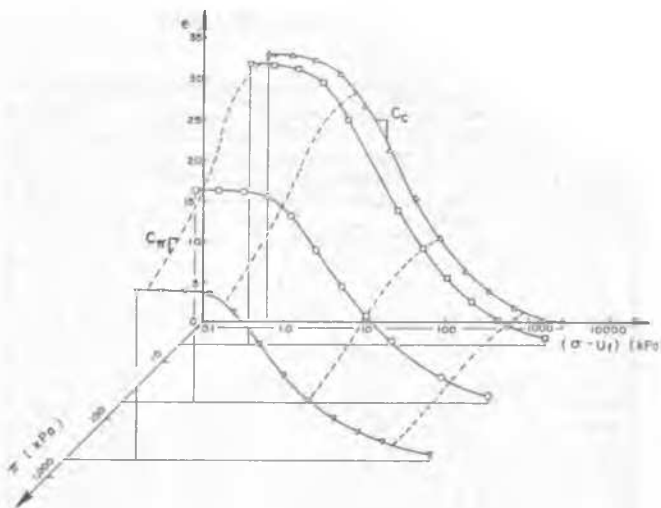(2) the variables can be theoretically justified,

Figure 2. Three dimensional constitutive surface for Na-montmorillonite as drawn from the data of Mesri and Olson (1971).

(3) the variables are operational in practice, and
(4) the variables that have characteristics acceptable within the definition of stress state variables.

$(R-A)$ is not a stress which can be directly measured in laboratory testing. In addition, the prediction of $(R-A)$ is possible only under ideal conditions. This is a severe restriction to the use of $(R-A)$ as a component of the stress state variable. Because of this, it may be necessary that a deduced quantity, which is more easily measured than $(R-A)$, be used.

The osmotic pressure concept relates the change in repulsive stress between clay particles, to the osmotic pressure difference between the interparticle fluid and the bulk external fluid. Mitchell (1962) suggested that "double layer interactions and the consequent repulsion between opposing particles are reflected by the osmotic pressure". The osmotic pressure is described as having two components; one associated with the free salt in the bulk solution and the other caused by the additional ions required to satisfy double layer requirements. The osmotic pressure of the bulk solution can be readily evaluated using samples of the pore fluid, however the difference between the osmotic pressure of the bulk fluid and that between the clay particles cannot be measured directly.

In most practical problems, the change of osmotic pressure is of more interest with respect to volume change and shear strength than the absolute value of the components of osmotic pressure. Consequently, it can be assumed that the osmotic pressure of the bulk solution can be used as an independent stress state variable. The osmotic pressure satisfies the requirements listed above because it is a measurable quantity which is theoretically related to the $(R-A)$ stress through the osmotic pressure concept.

6 CONCLUSIONS

The design of waste containment facilities requires that the behavior of soils subjected to

changing pore fluid chemistries be incorporated into conventional geotechnical analyses. The microscopic mechanistic conceptual models such the diffuse double layer theory and the osmotic pressure concept have provided valuable qualitative insight into the role that pore fluid concentrations have on soil behavior, however, it is unlikely that these theories can be applied in a quantitative manner into routine geotechnical design.

The macroscopic phenomenological model of stress state variables presented in this paper provides a framework which can be extended into conventional geotechnical analyses. Further work is required to verify the use of physico-chemical stress states (i.e., (R–A) or osmotic pressure) and to define the material properties associated with the constitutive relations for volume change and shear strength.

REFERENCES

Aylmore, L.A.G. & Quirk, J.P. (1962). The structural status of clay systems. Clays and Clay Minerology, 9, 104–130.

Bailey, W.A. (1965). The effect of salt content on the consolidation behavior of saturated remoulded clays. 162 pp., USAE Waterways Experimental Station, Vicksburg, Contract Rpt 3–101.

Balasubramonian, B.I. (1972). Swelling of Compaction Shale. Ph.D. Dissertation, 236 pp., Department of Civil Engineering, University of Alberta, Edmonton.

Barbour, S.L. (1987a). Osmotic Flow and Volume Change in Clay Soils. Ph.D. Dissertation, 255 pp., Department of Civil Engineering, University of Saskatchewan, Saskatoon.

Barbour, S.L. (1987b). The Role of physico-chemical effects on the behavior of Clay Soils, Proceedings of the 40th Canadian Geotechnical Conference, Regina, Saskatchewan, 323–342.

Barbour, S.L. & D.G. Fredlund. (1988). Mechanisms of Osmotic Flow and Volume Change in Clay Soils. submitted to Canadian Geotechnical Journal, June 1988.

Blackmore, A.V., & Miller, R.D. (1962). Tactoid size and osmotic swelling in calcium montmorillonite. Soil Science Society America Proceedings, 25, 169–173.

Bolt, G.H. & Miller, R.D. (1955). Compression studies of Illite suspensions. Soil Science Society America Proceedings, 19 285–288.

Bolt, G.H. (1956). Physico-chemical analyses of the compressibility of pure clay. Geotechnique 6(2), 86–93.

Chapman, D.L. (1913). A contribution to the theory of electrocapillarity. Philosophical Magazine 25(6), 475–481.

Chattopadhyay, P.K., (1972). Residual Shear Strength of Some Pure Clay Minerals. Ph.D. Dissertation, 340 p., Department of Civil Engineering, University of Alberta, Edmonton.

Dunn ,R.J. & Mitchell, J.K. (1984). Fluid conductivity testing of fine grained soils. Journal of the Geotechnical Engineering Divison, ASCE 110 (11), 1648–1665.

Fredlund, D.G. (1973). Volume Change Behavior of Unsaturated Soils, Ph.D. Dissertation, Unversity of Alberta, Edmonton, Alberta.

Fredlund, D.G. (1987). The stress state for expansive soils. Sixth International Conference on Expansive Soils, Lectures – Additional papers, Centre Board of Irrigation and Power, New Delhi, India, 1–9.

Fredlund, D.G. & Morgenstern, N.R. (1976). Constitutive relations for volume change in unsaturated soils. Canadian Geotechnical Journal 13(3), 261–276.

Fredlund, D.G. & Morgenstern, N. (1977). Stress state variables for unsaturated soils. ACSE Journal of the Geotechnical Engineering Division 103 (GT5), 447–466.

Gouy, G. (1910). Sur la constitution de la charge electrique a la surface d'un electrolyte. Anniue Physique (Paris) 9(4), 457–468.

Kenney, T.C. (1967). The influence of mineral composition on the residual strength of natural soils. Proceedings of the Oslo Geotechnical Conference, Vol. 1, reprinted in NGI Publ. No. 76, 37–43.

Lambe, T.W. (1960). A mechanistic picture of shear strength in clay, Proceedings of the ASCE Research Conference on Shear Strength of Cohesive Soils, University of Colorado, Boulder, Co., 555–580.

Mesri, G. & Olson, R.E. (1971). Consolidation characteristics of montmorillonite. Geotechnique 21 (4), 341–352.

Mitchell, J.K. (1962). Components of pore water pressure and their engineering significance. Clays and Clay Minerals, 162–184.

Mitchell, J.K. (1976). Fundamentals of Soil Behavior. 422 pp., John Wiley and Sons, New York.

Morgenstern, N. & Balasubramonian, B.I. (1980). Effects of pore fluid on the swelling of clay-shale. Proceedings of the 4th International Conference on Expansive Soils, Denver, 190–205.

Stern, O. (1924). Zur Theorie der elktrolytischen Doppelschriht. Zeitschrift Electrochem 30, 508–516.

Terzaghi, K. (1936). The Shearing resistance of saturated soils. Proceedings of the First International Conference on Soil Mechanics, Vol. 1.

Truesdell, C. (1966). The Elements of Continuum Mechanics. Springer-Verlag, Inc., New York, N.Y.

Warkentin, B.P., Bolt, G.H., & Miller, R.D. (1957). Swelling pressure of montmorillonite. Soil Science Society of America Proceedings 21, 495–497.

Warkentin, & Schofield. (1962). Swelling pressures of Na-Montmorillonite. Soil Science 13, 98–105.