Water-mineral interaction in hydromechanics of clays exposed to environmental loads: a mixture theory approach

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Water-mineral interaction in narrow interstices (< 30 Å (1 Å = 0.1 nm)) in dense, saturated clays is discussed in view of recent experimental findings and molecular dynamics simulations. Consequences to the macroscopic behavior are considered. A mixture theory for two interacting constituents is developed. Effects of temperature and chemicals are discussed. A postulate of mass transfer of adsorbed water from solid to fluid fraction caused by thermal or chemical load is then discussed. Theory of plasticity of clays affected by heat or chemicals is developed to deal with the effects of thermal and chemical consolidation.

Key words: hydraulic conductivity, effective stress, environmental loads, thermo-chemo-plasticity.

L'interaction eau-minéral dans les interstices étroits (< 30 Å (1 Å = 0.1 nm)) d'argiles densées saturées est discutée à la lumière des résultats expérimentaux récents et des simulations de dynamique moléculaire. Les conséquences sur le comportement macroscopique sont prises en considération. Une théorie de mélange pour deux constituants interagissant est développée. Les effets de température et des constituants chimiques sont discutés. Un postulat de transfert de masse d'eau adsorbée de la fraction solide à la fraction fluide causé par la chaleur thermique ou chimique est alors discuté. Une théorie de plasticité des argiles affectées par la chaleur ou les produits chimiques est développée pour traiter des effets de consolidation thermique et chimique.

Mots clés : conductivity hydraulique, contrainte effective, charges environnementales, thermo-chimio-plasticité.


Introduction

A basic element in the design of a long-life engineered or natural clay barrier is prediction of the long-term performance of the barrier. To perform such a prediction, both the knowledge of physical and mechanical properties of clays and the access to a mathematical model able to simulate quantitatively these properties are necessary. This paper deals with such a model based on the mixture theory. This study focuses on the role, played by environmental loads in combination with mechanical loads in the performance of the barriers. In particular, the environmental loads affect the behavior of adsorbed water in clays and, through that, many other clay properties. Recent findings in surface physicochemistry confirm earlier hypotheses by Low (1979) that water in nanoperces (< 10−10 m) corresponding to the size of clay interstices have properties very different from the properties of bulk water.

In this paper the nature of water-clay interaction is analyzed on three levels: molecular, microscopic (particle), and macroscopic (continuum). The goal is to develop a macroscopic, mixture-theory model, including constitutive laws of the response to thermal and chemical loads, using results of molecular and microscopic experiments and models.

Basic observations and hypotheses

Models commonly used in soil mechanics and physics, such as Darcy's law, consolidation theory, elasticity or plasticity, heat conduction, and diffusion of chemical species, are usually employed separately, i.e., as decoupled.

However, more than any other geotechnical structure, clay barriers require a global, combined hydromechanical approach. In fact, the mechanical failure of a clay barrier depends on effective stresses. These depend on water pressure, temperature, and perhaps electrochemical forces. In turn, the buildup of water pressure depends, among other factors, on permeability. However, permeability is a function of skeleton porosity, and changes in porosity, through volumetric strai, depend on effective stress. On the other hand, the hydraulic failure of a clay barrier results from critical changes in porosity. These in turn depend on permanent chemistry and on effective stress (Quigley and Fernandez 1991).

In addition, an electrochemical interaction between solids and water takes place in clay on a microscopic scale. As a result of this interaction, water present in clay takes on four different forms (Bennett and Hubbert 1986; Szczyzowska 1990) (Fig. 1). (1) Free or bulk water, which is able to flow due to hydraulic gradient at room temperature. (2) Interlayer adsorbed water, enveloping clusters of smectite, illite, and single particles or possible clusters, when formed, of kaolinite. This water is restricted from flow in normal conditions (Olsen 1962; Cheung et al. 1987; Kemper et al. 1964). (3) Intracrystallite adsorbed water, associated with interlamellar surfaces in smectites, the area of which can be determined by special techniques. At the low porosities discussed here, only a few molecular sheets of water can fit in the available interlamellar space. The interlayer water cannot flow in ambient conditions. (4) Finally, there is structural water or hydroxyl, which is a part of the structural lattice of the clay mineral. This water does not leave the solid below 350°C. The first three forms of water are of main interest here.

Environmental loads, namely temperature, changes in water chemistry, irradiation, and chemical loads from haz-

to know the properties of the constituents and their possible interaction. For clay-s, the mixture may, moreover, be assumed as binary (i.e., with an equal temperature in all constituents). This is based on the fact that, in general, the main interaction in silts and clays is negligible in comparison with conduction (Buehrle and Martino, 1940).

In what follows, the mixture constituents will be defined, their four basic components of the mixture theory will be dealt with for each constituent, and the mixture laws for the constituents will be presented. In particular, a novel chemoplasticity for clays will be presented. The constitutive parameters are assumed to depend on variables pertaining to a given constituent only, according to the principle of phase separation developed for multiphase flow theory (Drew and Segel, 1971) (see also Nakaike and Tsuchiya, 1981). This is different from the equilibrium principle, which requires a dependence of the behavior of a constituent on all the variables describing all other constituents (Truesdell 1969, 1986).

Constituents in clay-water mixture

Cut as a separate phase will not be considered here. Even without any gas, clay might be perceived as a three-constituent mixture because of the presence of adsorbed water. Not all properties of adsorbed water are known with certainty, but those that are known are distinctly different from those of bulk water. First of all, at least the material conditions, a part of the adsorbed water is not able to flow and thus will be referred to as immobile water (Lemper et al., 1964).

Further considerations are restricted to high-density clays, such as those used in radioactive barriers, for which bulk density exceeds 1.5 Mg/m³. This limitation is very important because it excludes from consideration clay suspensions, clays, and low-density clay soils. In these latter materials water is predominantly located in large voids, where a fully developed DDL may form. In contrast, in clays with high bulk density, a substantial fraction of volume of their water is in small interisomer layers. Only a minor fraction of the water is located around the external surfaces of clusters of needle-like secondary hydrate layers. For artificial Na-montmorillonite, Pine and Homeck (1960) estimate that at saturation and a bulk density of 1.9 Mg/m³, more than 60% of the water is immobile. For natural Boom clay (minimally with 22% anisotropy), 19% ilite, 29% kaolinite, and 39% quartz at a total water content of 13%, the ratio of interlayer to total water content has been calculated to be 24, 37, and 49%, respectively, for two, three, and four monomolecular layers of interlayer water (Bald et al., 1991). Thus, from a quarter to a half of water behaves more like solid than fluid in such clays.

For the above reasons saturated clay will be labeled as what follows as a two-constituent mixture. The constituents will be referred to as solid and fluid, with the immobile water attributed to the solid phase.

Thus, the volume fraction, and, respectively, are defined as

\[ n_f = n_s + n_i \]

\[ n_s + n_i = 1 \]
where $n_1$ and $n_2$ are volume fractions (or porosities) of immobile and mobile water, respectively; and $n_3$ is the volume fraction of the clay mineral:

$$n_1 = \frac{V_1}{V}, \quad n_2 = \frac{V_2}{V}, \quad n_3 = \frac{V_3}{V}$$

where $V_1$ and $V_2$ are the volumes of immobile and mobile water, respectively; and $V_3$ is the volume of clay mineral particles, and $V$ is the total volume of the element. Using the above volume fractions, the partial bulk densities $\rho'$ and $\rho''$ are defined for fluid and solid constituents, respectively, as follows:

$$\rho' = n_2 \rho_{2f}, \quad \rho'' = n_3 \rho_{3c} + n_1 \rho_{1w}$$

where $\rho_{2f}$, $\rho_{3c}$, and $\rho_{1w}$ are specific densities of immobile and mobile water and clay minerals, respectively.

To take into consideration changes in adsorbed water, the mass-transfer approach has been developed (Hussqvel 1988). The term mass-transfer refers to the transfer from the solid to the fluid constituent of immobile water, which becomes mobile as temperature increases or pore-fluid chemistry changes (Hussqvel 1999; Hussqvel and Ma 1991).

Figure 3 shows the mass-transfer coefficient $K$ for water and fluid volume fractions $n_1$ and $n_2$ are variable. The variations of the volume fractions are related to the mass transfer of the immobile water and to strain, through a mass-conservation law. The mass transfer is defined through a constitutive law.

The specific density $\rho'$ [3] is in principle also variable and are defined through usual physical laws. As a consequence of the above definitions, all properties of the solid fraction are variable. They are determined as weighted averages of the specific properties of the clay mineral and the immobile water, proportional to the volume fractions. Thus, although immobile water is not explicitly considered as a separate constituent, its volume fraction and other specific properties should be known to evaluate the properties of solid constituent.

Volume fraction and density of immobile water

In this section we review recent findings concerning volume fraction and properties of immobile water. The distinction between immobile and mobile water is based on the difference in velocities of these particles. In practice, there are no means to determine this difference from a macroscopic experiment. What is determined commonly is water content by drying clay in an oven at 105°C refers mainly to the mobile water, but also it includes a good part, but not all, of the immobile water. Derjaguin et al. (1986) believe that at temperatures as low as 70°C, the water in small intertubes (50 Å) loses its special structure. However, experiments by Pusch (1987) and Pusch and Grive (1989) suggest that clay at this process coexists through 250 up to 260°C (see also Gram 1968 and Keddi 1971, p. 47). Thus, for present purposes, the classical chemical methods for measuring water content is inconclusive. Heating to a higher temperature can yield the total volume of water, but the fraction of mobile water will remain underestimated.

A microstructural analysis can be used to obtain an estimate of the volume fraction occupied by the immobile water. In the past decade, growing experimental evidence has accumulated, showing that theory of D3H3 describes accurately the behavior of adsorbed water only at interparticle distances greater than 50 Å and low salt concentrations,
for which Debye-Hückel theory holds (Israelachvili 1985; Torrie and Valleau 1980; Sposito 1984; Ninham 1981) (Fig. 2).

In the interstices smaller than 50 Å, solvation forces become dominant close to the surface. This is because the discrete molecular structure of a fluid makes the short distance intermolecular pair potential different from that obtained from any continuum theory. The solvation phenomenon is governed by the geometry of molecular packing imposed by the rigid boundary of solid platelets (Fig. 2).

If the separation between the particles is less than 8–10 molecular diameters (20–26 Å), the entire interparticle fluid acquires a special structure and its properties and the stress transmission assume a different aspect (Fig. 3) (Israelachvili et al. 1988). Numerical simulations to explain the results of the experiments by Israelachvili and others were performed using the Monte Carlo method and molecular dynamics on Lennard–Jones (LJ) liquid (e.g., see Allen and Tildesley 1987). The main results concern the compression of the liquid between two parallel walls and its shear. The simulations indicate that the density of liquid oscillates with varying distance from the solid surface (Fig. 4) (Schoen et al. 1987). It may be seen, for example, that in the pore space 16.5 molecular diameters large, one quarter of the pore width on each side is occupied by a liquid with average density much higher than the bulk water.

Skipper et al. (footnote 2) performed Monte Carlo simulations of the behavior of montmorillonite. The system they examined comprised a clay solid layer, 64 water molecules, and 8 Na or 4 Mg interlayer cations, being a part of periodically repeated structure with 20% water content. The unit was subjected to uniaxial stress of 1 MPa. Six different molecular interaction potentials: viz., water–water, water–cation, water–cation, water–clay, cation–cation, and clay–clay have been considered related to attractive London forces or dispersion forces, short-range repulsion, and Coulomb force between charged sites. The obtained layer spacings were only 3% smaller than the known experimental values. In 14.3Å Na smectite, the cations were binding to the clay surface and the average interlayer water density obtained

\[^{2}\text{N.T. Skipper, K. Refson, and J.D.C. McConnell. Monte Carlo simulations of Mg- and Na-smectites. In preparation.}\]
by Skipper et al. (footnote 2) was 1.14 ± 0.04 g/cm³. In 14.7-Å Mg smectite, the structure of the interlayer water is heavily dominated by the centrally located cations. The average density of the interlayer water in Mg smectite was found to be 1.38 ± 0.04 g/cm³. Skipper et al. (1991) examined the influence of the external pressure and water content. Although the numbers obtained from these early simulations may be further refined, they do confirm the findings by Schoen et al. (1987) of localized peaks of density far exceeding unity in immeasurable water. In contrast, for Na montmorillonite with water contents higher than 78%, Anderson and Low (1983) and Low (1979) found the adsorbed water to be less dense than bulk water (see also Martin 1962). Early experiments performed by Kemp et al. (1964) to evaluate the mobility of adsorbed water as opposed to bulk water indicate that at least two molecular layers of the solid boundary have reduced mobility. Numerical simulations of water mobility in montmorillonite clay were performed recently by Refson et al. (footnote 3) by molecular dynamic techniques on the same model system as above, at constant-volume conditions. Water molecules within the hydration shell have very limited mobility. Free molecules of water, still present in the liquid, have much higher mobility. The computed value of overall diffusivity is one-tenth of the corresponding value for bulk water. Earlier tests on Na montmorillonite by Adams et al. (1979) and tests by Drueke and Carlson (1983) and Carlson (1985) have also shown lower diffusivity of clay water.

In conclusion, in interlayers larger than about 10 molecular diameters, there is a member (two to four) of molecular layers which have highly different fluid properties from bulk liquid. In interlayers smaller than 7-10 molecular diameters, the fluid properties of the water are different from the bulk water. In particular, the shear strength and viscosity are much higher. In the following sections, this water will be considered immobile.

Mass-conservation equations

The mass-conservation principle is believed in mixture theory to apply to each constituent separately and to the mixture as a whole (e.g., see Tresidder 1986). An essential feature of the mass balance in clays is the mass transfer between the constituents. For each constituent, the mass-conservation law states

$$\frac{\partial \rho_i}{\partial t} + \rho_i \nabla \cdot \mathbf{v}_i = \Phi_i$$

where $\nabla \cdot \mathbf{v}_i$ is the convective flux of mass. The variables $\rho_i$ and $\mathbf{v}_i$ are the concentration and velocity components of fluid and solid, respectively, the variable $\Phi_i$ is the mass transfer toward solid and fluid phases, respectively, interrelated through Tresidder’s (1969) equation

$$\frac{\partial \rho_i}{\partial t} + \rho_i \nabla \cdot \mathbf{v}_i = 0$$

Equation (2) assumes that the mass can be generated in one constituent through any process, without an equal mass

Fig. 5. Decrease of short-range force $f_i$ vs. separation $R_i$ for different temperatures. The force is normalized with surface curvature radius $R$. (From Ciascone et al. 1986.)

In classical approaches such as three-dimensional consolidation theory, $\Phi_i$ reduces to the statement that the gradient of the solid velocity can be expressed and measured as the volumetric strain rate of the whole material. The same equivalence stay be reached in mixture theory (Ma and Husek 1992) under the following assumptions: (i) the velocity of immobile water is equal to that of the clay mineral particles, (ii) the mass transfer affects immobile water only, and (iii) specific densities of the clay minerals are constant. The latter assumption is consistent with a further requirement that the whole deformation of the soil is determined by a phenomenological constitutive relationship, without any distinction between the contributions of immobile water and mineral.

In the present context, it must be underlined that only the flow channels corresponding to mobile water are available for flow. This, in defining the discharge velocity $q_i$, the true velocity of water particles with respect to solid particles is scaled by a factor corresponding to the effective porosity of mobile water $\eta_i$. Therefore,

$$q_i = \eta_i (\mathbf{v}_i - \mathbf{v}_f)$$

Thus, the equation for mass conservation for the bulk fluid is

$$\frac{\partial (\rho \mathbf{v}_f)}{\partial t} + \rho \nabla \cdot \mathbf{v}_f = \Phi_f$$

This equation links the change in mobile water porosity and the solid volume change with the mass-transfer rate of immobile water. The velocity of solid particles is often neglected as small. Finally, the balance of mass in the usual form needs to be satisfied for the whole medium, with the bulk density defined as \( \rho = \rho^1 + \rho^s \), if condition [6] is fulfilled.

**Degeneration of immobile water (mass-transfer hypothesis)**

In this section we discuss the central hypothesis of this paper that environmental loads can substantially reduce the volume fraction of immobile water. We first review data from the literature then formulate the hypothesis mathematically.

**Sensitivity of clays to environmental conditions**

Clay barriers by definition are subjected to changes in environmental conditions. In nuclear repositories, these include heat and irradiation. In the case of hazardous waste disposal and spills, the changes consist of an inflow of organic and inorganic chemicals, and often temperature changes as well.

**Heat**

For smectites, microscopic studies by Pusch (1987) and Pusch and Givens (1988) show that heating up to 150°C induces reversible dehydration of the platelets and consequent contraction of stacks, which leaves larger voids between them. Between 150 and 200°C this process is enhanced and becomes at least partially irreversible, supposedly due to cementation by precipitated silica, which scales the tips of interlayer channels. Thermal dehydration of clusters of smectite is a widely accepted concept in sedimentation theories (e.g., Rieke and Chilingarian 1973). It is believed that smectite under pressure for an extended period of time becomes altered to illite. This has been reported in the laboratory (Khitarov and Pugin 1966). As smectite is altered to illite, the intracrystall water becomes free water, with the consequent changes in water density (Powers 1967; and Burst 1969; Wintzen and Bauer 1934). Recent findings on water behavior in interstices smaller than about 40 Å suggest a breakdown of the special structure of this water, which becomes more like bulk water at about 70°C (Derjaguin et al. 1986; Derjaguin and Chraer 1989). Similar breakdown was obtained at an even lower temperature (37°C) in a model liquid by Claesson et al. (1986) (Fig. 5). Currently two hypotheses explain such a breakdown. Mitchell et al. (1983) and Staples and Tiddy (1978) suggest a thermal breakdown of the hydration shells. Kjellander et al. (1982) and Claesson et al. (1986) argue that at higher temperatures both repulsion and attraction grow, but attraction becomes dominant. These studies were conducted on various model materials, and thus the value of temperature at which such a switch-over in clay water may occur may be different.

Macroscopic experiments on normally consolidated clays containing smectites show a significant compression upon heating. However, overconsolidated clays showed an initial expansion, followed at higher temperatures by a compression (Fig. 6) (Baldi et al. 1991; see also Hueckel and Baldi 1990). During subsequent cooling the compression continued, and a net irreversible deformation remained after the completion of a closed temperature cycle. The findings confirm earlier results of Yong et al. (1963), Sheriff and Burrous (1969), and Laguros (1969). A thermal cycle of heating and cooling leads to an increase of the apparent preconsolidation pressure in normally consolidated clays (Plum and Elwig 1969; see also Mitchell 1973). According to the thermo-
plasticity theory, seasonal temperature cycles may produce the effect that no natural clay, except very fresh sediment, can be normally consolidated after one heating-cooling cycle (see also Schmertmann 1991). In moderately and heavily consolidated clays, the preconsolidation pressure decreased with temperature (Tisdfor and Saffors 1989). A review of effects of heating up to 550°C on the mechanical properties of clays was given recently by Wang et al. (1990).

Permeability of bentonites may grow due to heating-bentonites up to two orders of magnitude per 100°C (Pusch 1986). This is four times more that could be expected simply from the thermal change in water viscosity (see also Mitchell 1975; Ma and Huczko 1992). Preliminary studies with molecular dynamics were performed for montmorillonite (Reeves et al., footnote 3). At 67°C the self-diffusivity coefficient increases up to 89% in Mg smectite (Fig. 7). The most characteristic phenomenon observed at 67°C is a jump of cation, accompanied by the jump of hydration shell mole-
cules, leading to this increasing diffusivity. A model of dif-
fusion through jumps has been previously analyzed and investigated experimentally by incoherent quasi-elastic neutron scattering by Cebula et al. (1981), who obtained, respectively, one-eighth and one-quarter of the bulk water diffusion coefficient for one-layer and three-layer samples.

In illite, a considerable loss of water is known to occur due to dehydration below 100°C, due to the possible pres-
ence of some residual interlayer water (Grím 1968). Heating-
induced consolidation was also observed in illite (Pawel
ewell 1967; Campanella and Mitchell 1968; Plum and Eirig 1969; Houston and Liu 1987; Bakli et al. 1988). Some further, small consolidation was observed during subsequent cooling by Campanella and Mitchell (1968).

Kaolinite shows no dehydration in temperatures below 400°C due to absence of any interlayer water (Grím 1968). However, in a heating experiment, Pontida clay with 20% kaolinite and 25% illite has shown thermal consolidation (Bald et al. 1988). Campanella and Mitchell (1968) have also shown that kaolinite consolidates thermally.

Chemical loading

Olson and Mersi (1970) and Sridharan and Venkatapra Rao (1973) conducted experiments with high-porosity clays in which water was replaced by a number of different fluids with different dielectric constants. These authors concluded that clay compressibility depends primarily on the ability to form a DDL around solid particles. They also found that compressibility is very sensitive to DDL properties in smec-
tites, much less so in illites, and almost not at all in kaoli-
nites. Sridharan and Venkatapra Rao (1973) suggest that the mechanism of compression in smectite is governed by long-range repulsive forces due to development of DDLs, whereas in kaolinite compression depends on interparticle shearing resistance. The main chemical variables that control the response of illites and nonmontmorillonites in compression are (i) surface charge density, (ii) valency of the adsorbed cations, (iii) dielectric constant and dipole moment of the pore fluid, and (iv) concentrations of the electrolytes in the free pore fluid (Olson and Mersi 1970).

As far as shear strength is concerned, no significant effect was found for electrolyte concentrations in kaol-
nites and montmorillonites. However, a distinct strength decrease was caused in sodium illite. Increases in cation valence invariably increase strength (Olson 1974). Presum-
ably, a well-developed DDL reduces the friction at contacts between strong clusters in illite. Low strength and the lack of any effect of counterion changes in sodium montmoril-
onite were attributed to the low mechanical strength of the flaky particles themselves. The effect of a change in pore fluid on strength was investigated by Sridharan and Venkataappa Rao (1973). The shear box strengths in terms of friction angle and cohesion intercept were all increasing with decreasing dielectric constant. The effect was remark-
able at dielectric constants less than 2. Kaolinite appears to be more sensitive to dielectric constant drop than montmoril-
onite. These results suggest that shear strength is much less affected by interlayer water than by externally adsorbed water, which is prominent in illites and in kaolinite. How-
ever, it should be noted that all the above experiments were performed on clays at initial void ratios between 2 and 4.

A fundamental question concerning the effectiveness of a clay barrier is how chemical loading and stress change hydraulic conductivity. The main deformation mechanisms resulting from the interaction of chemicals with clays are swelling, flocculation, and macroscopic craking (e.g., see Quigley et al. 1988; Fernandez and Quigley 1991). Removal of adsorbed water by a 100% substitution by an organic liquid may increase hydraulic conductivity by up to two to three orders of magnitude if there is no stress applied, as in a rigid-well permeator (Anderson et al. 1985). How-
ever, at a compressive stress studied in a flexible-well per-
meator, hydraulic conductivity may decrease up to two orders of magnitude. It is generally hypothesized that these very significant differences are related to the fate of the free void space left after the collapse and removal of adsorbed water. For instance, the substitution of water by heptane or carbon tetrachloride in (i) illite, and (ii) chloride or lactate causes, respectively, a 660- and 7.5-fold growth of hydraulic conductivity in the absence of external stress, and conversely a 500- and 0.62-fold drop under a moderate stress, (Bowders and Daniels 1967). Mitchell and Maasue (1987) give a thorough review of various effects of inorganic and organic chemicals on clay hydraulic conductivity as applied generally to liners. Inorganic, when they increase concentration and cation valence, cause flocculation and reduce swelling, leading to an increase in hydraulic conduc-
tivity. Organics, more important from the point of view of the human environment, are the focus of concern. They may

![Graph showing hydraulic conductivity changes.](image-url)
The mass transfer due to chemical loads is believed to affect predominantly external surfaces of clusters. Many pollutants are not able to penetrate into the intermolecular space in dense clays, both for geometrical reasons (the molecules are too large) and for physicochemical reasons. Also, it should be remembered that our objective is to quantify the change in volume fraction of mobile and immobile fluids. Thus, for example, the molecular adsorption of the guest liquid, associated with the replacement of adsorbed water, does not contribute to mass transfer in our sense. In addition, mass transfer is highly complicated by, among other factors, the miscibility of chemicals, and water, the interaction of clay with the chemicals and by the molecular diameter of the chemicals when compared with that of water (Green et al. 1983; Mitchell and Mason 1987; Fernandez and Quigley 1985, 1987; Yong and Rao 1991; Sawhney et al. 1990; Budha et al. 1990).

However, there are a number of circumstances in which it seems that a variable dielectric coefficient is a predominant factor in permeability changes (Budha et al. 1990). In such cases, if all other environmental variables are kept constant, the mass transfer may be expressed through a linear relationship between rates of mass transfer and dielectric coefficient:

$$\dot{\rho}_b^d = \frac{D^*}{D^*(T)} (n^c - n^S(0)) \quad D^* \leq D, \quad T \leq T_d$$

where $D^*$ and $D$ are dielectric coefficients, respectively, of water and of the fluid mixture currently permeating clay, defined as $D = cD^* + (1 - c)D^*$, where $c$ and $D^*$ are, respectively, the permittance concentration and the dielectric constant of the guest liquid; the integer number $t$ is the number of irremovable layers of adsorbed water from the mineral wall; $S^*$ is the specific surface area available for the molecules of the guest liquid; and $n^c$ is the value of the initial volume fraction accessible by the given type of guest molecules.

Equations [9] and [10] clearly involve drastic simplifications. Further effort is necessary to establish more physically substantiated forms of these relationships, related to particular sorbing mechanisms, (e.g., see van Genuchten and Wierenga 1976; Barone et al. 1988).

Linear momentum conservation

In mixture theory, it is assumed that the linear momentum balance must hold separately for each constituent and for the whole medium. Also, the additivity of partial stresses is usually explicitly assumed. In the balance, the interaction forces between the phases and the linear momentum supply resulting from the mass transfer are also included. Thus for a constituent $\alpha$, the balance reads

$$\sigma_{ij}^\alpha + \rho_\alpha \ddot{u}_i = -p_\alpha \delta_{ij} - \rho_\alpha \frac{D^*_\alpha}{D} \dot{\rho}_b^\alpha = 0$$

where $\sigma_{ij}$ is the stress component, $\delta_{ij}$ is the gravity component, and $\dot{\rho}_b^\alpha$ is the interaction force component.

The interaction forces are then postulated to be the sum of a term proportional to water specific discharge $q$, a term dependent on effective porosity and bulk water pressure gradients and a term proportional to the interconstituent mass-transfer rate (following Bowen 1975; Trusdell and Taplin 1969; Høkmark 1990).
Molecular shear behavior of interlamellar fluids

When the separation between the solid particles is less than 8-10 diameters of water molecule, the interparticle water acquires a special structure, and so does the transmission of shear stress between the particles. In experiments by Israelachvili et al. (1988), two mica surfaces were slid under different normal forces and with different velocities in the apparatus shown in Fig. 10. Sliding takes place by forcing in the fluid the formation of a discrete number of molecular layers. There is a critical shear stress required to initiate the sliding. This critical shear stress depends on the number of the molecular layers. For example, it is two times larger for two layers than for three layers (Fig. 11). If the number of layers during flow is constant and low, the shear stress is also constant and does not depend on velocity of motion. None of these features can be exposed in a Newtonian viscous fluid. The shear viscosity in such small intercalaries (1-2 molecular layers thick) is five to seven orders of magnitude higher than in the bulk fluid, the properties of which are approached when the number of layers exceeds seven.

Numerical simulations using molecular dynamics (Schoen...
\[ p_i = \frac{n \gamma_i}{k} \nu_i - \rho_i B_i \cdot \nu_i = n \mu \nu_i = n \mu \nu_i \]

where \( \nu(T) \) is dynamic viscosity of the fluid, and \( B_i \) and \( \nu_i \) are the velocity and mean velocity over the mixture, respectively. Thus, the linear momentum balance equation for fluid \( n_i \) reduces to the following:

\[ \dot{q}_i = -\frac{r_e}{r_e} \left( \dot{u}_j + \rho_j g \right) \]

Thus Darcy’s law is recovered.

Permeability

Permeability of nonfractured, dense clays is constant, via Kozeny–Carman equation derived from Poiseuille flow equation, to the effective porosity (Cheung et al. 1981) relating only to the channels available for flow, and thus to the mobile water porosity \( n_1 \) (Olsen 1963). The relationship between the two variables is given as:

\[ k = \frac{1}{r_{np}^2 S_m (1 - n_2)^3} \]

where \( S_m \) is the specific surface area relative to the mobile water space; \( r \) is a shape factor, usually taken as equal to 2.5; and \( T \) is tortuosity factor, usually taken as 1.414. The mobile water porosity \( n_1 \) on which the permeability depends is related in turn through the mass-balance equations [3] and [4] to the mass transfer and deformations of the interstitia produced by stress or temperature changes. Cheung et al., (1987) evaluating \( n_1 \) suggested that pressures producing flow must be larger than osmotic pressure.

To calculate an approximate value for the current permeability in practical applications, it is common practice to use a reference porosity value \( n_0 \) determined in an undisturbed configuration, characterized by an initial value of bulk water porosity \( n_2 \):

\[ k = k_0 \left( \frac{n_2}{n_2} \right)^3 \]

Effective stress in clays

A fundamental assumption needs now to be made about the interpretation of the partial stresses in the solid and fluid phases. It is well established that the area of the actual contact between solid particles in most soils is less than \( 1\% \) of the total area of the particles (Skempton 1963). Thus, in considering the partial stress in the bulk water, the customary definition will be adopted (see Bazant and Krizek 1975; Kowalski 1978) by referring water pressure to the effectively affected area. Assuming that the area fractions in the mixture are proportional to the volume fractions (Morland 1972), the mobile fluid porosity \( n_1 \) is used as the scaling factor, so

\[ \sigma = n_1 \mu \sigma + \sigma' + (1 - n_1) \mu \]

where \( \sigma, \sigma', \sigma'' \) are, respectively, the isotropic stress in the solid and the fluid, the effective isotropic stress in the clay skeleton, and the isotropic stress in the whole medium. Thus, by summing up the above-defined partial stresses, the familiar Terzaghi’s (1922) effective stress principle is recovered:

\[ \sigma = \sigma + \sigma' = \sigma + \mu \]

In Biot’s consolidation theory the contribution of the partial stresses to the global stress is affected by the compressibility of the solid mineral. However, according to Skempton (1963), the effect of compressibility is negligible for clays.

The actual problem in clay mechanics is the role of the electrochemical forces in carrying the total load. A constant process, often arises centered over the fact that electrochemical repulsion may reduce contact forces in the skeleton, and in consequence may reduce the shear strength of interparticle contacts. This may lead to failure of the skeleton at much lower load than would be predicted without taking the electrochemical forces into account. Equations [11] and [12] are consistent with the assumption that clay is a two-constituent medium. However, the physical meaning of the variable of the effective stress \( \sigma' \) remains to be defined.

In defining the effective stress it may be convenient to refer to three different kinds of interparticle contacts that are encountered in various clay minerals depending on various geological and environmental conditions. These are close and distance face-to-face (cFF and dFF) contacts and edge-to-edge (EF) contacts, as represented in Fig. 8. In this context, Hueckel (1992) has identified three linear mechanical stress-strain models that may be derived for saturated clay from various effective-stress definitions following, respectively, (i) Lambe (1960) and Mitchell (1962) (Fig. 9a); (ii) Siddharthan (1968), Siddharthan and Rao (1973), Balasubramaniam (1977), and Morganstein and Bansubramaniam (1980) (Fig. 9b); and (iii) Bov (1956), Lamba (1969), Nagarat, and Jayadeva (1981), and Graham et al. (1989) (Fig. 9c). In these models the interparticle contact stress \( \sigma' \), and the net repulsive less attractive force \( \sigma - A \) are connected in series or parallel in two different arrangements, being in addition set in parallel with the bulk water pressure \( \sigma' \).

From an analysis of the deformation induced in clay by mechanical actions or changes in the permeant chemistry, Hueckel (1992) concluded what follows. The series model (Fig. 9c) seems to be appropriate if cFF and dFF contacts are dominant. A consolidation process can be understood as a progressive conversion of a number of EF contacts into FF (face-to-face) contacts, so a dense clay has a predominant population of FF contacts, as discussed by Resendez (1965). The series model incorporates the Terzaghi’s principle and additionally a physicallychemically dependent deformation law. According to this law, the volumetric deformation of the clay porous skeleton and that of adsorbed water add up to yield the deformation of the solid phase. This sum, in turn, corresponds to the change in bulk water volume. The strength also depends explicitly on chemical variables and temperature. For further analysis of chemical effects on effective stress see Hueckel (1952). In the following section, constitutive laws are proposed in which the above-outlined series model is adopted to describe strain as a sum of the environmentally and stress-induced strains.
et al. 1987, 1989) confirm that liquids at close separation of solids flow in ordered layers at much higher viscosity. An abrupt transition from liquid- to solid-type of flow occurs by the formation of block-like ordered structures when separations are less than 6 molecular diameters. Values of predicted shear stresses at yielding were similar to experimental values. They also were dependent on the number of layers (Schoen et al. 1989; Cusman 1990) (Fig. 12). However, as opposed to the experimental studies outlined here, the numerical simulations showed that shear stresses would abruptly decrease at a critical value, and an entire layer of molecules would leave the pore, after which the remaining layers would restructure themselves. This difference is explained by the condition of constant separation (no dilatancy), assumed in the numerical work. Constant normal force conditions, allowing variation in separation, were imposed in the experiments.

In conclusion, Gee et al. (1990) proposed a phenomenological equation for friction in narrow spaces in which the total shear resistance is composed of a part (S_r) due to the (internal) adhesion force between the two surfaces and another part due to the externally applied load:

\[ \tau^* = S_r + C \sigma^* \]

where \( \tau^* \) and \( \sigma^* \) are the total shear and normal stresses, respectively, at the contact (at the particle scale). The most important conclusion is that the \( S_r \) identified as internal adhesion depends on the number of molecular layers of fluid (Homola et al. 1989; Gee et al. 1990). The frictional coefficient \( C \) depends on atomic granularity of the surfaces and on the size, shape, and configuration of the liquid molecules in the pore. The order of magnitude of such frictional stress is \( 2 \times 10^7 \) N/m². It should be emphasized that only some of the results quoted were obtained for water. Therefore their application
It is understood that the partial stress in the clay mineral phase is equal to that in adsorbed liquid, as in the series model in Fig. 9c. This stress will still be called effective stress \( \sigma_e \). Also, in agreement with this model, strains generated by environmental loads will be added to those due to mechanical load. The reversible (elastic) strain is defined in the form similar to that in thermoelasticity theory:

\[
\varepsilon_e = \frac{1}{1 - \nu} \sigma_e - \alpha_e(\Delta T) + \beta \Delta D + \gamma \Delta c_v + \ldots
\]

where \( \Delta D \) is the elastic bulk modulus depending on the total accumulated mass transfer; and \( \alpha_e, \beta, \gamma \) are, respectively, the cubic thermal expansion coefficient, the flocculation coefficient, and the osmotic consolidation coefficient. All describing their respective reversible parts of volume change. In the above equation a gradual replacement of water with a lower dielectric constant fluid is described by a decrease in the resultant dielectric coefficient. The dependence of thermal expansion coefficient on effective stress in clay and methods of its determination have been studied in detail by Baldi et al. (1988). A dependence of the other phenomena such as flocculation and osmotic consolidation on effective stress is not known and requires experimental examination.

The emphasis in this section is placed on the irreversible effects of environmental loads. Plastic (nonrecoverable) consolidation strain at constant effective stress is an initially elastic stress range has been observed to result from (i) an increase in temperature (e.g., Campanella and Mitchell 1968; Baldi et al. 1987; Huczkel and Baldi 1990), (ii) an increase in ionic concentration or volume (e.g., Olson and Meny 1970; Baldi and Fredlund 1989); or (iii) a decrease in dielectric constant (e.g., Slichter et al. and Vugtenberg and Rao 1973; Fernandez and Quigley 1991). It is postulated here that there is a common mechanism in these types of consolidation which involves a degradation of the adsorbed water, with some of it becoming, in effect, mobile. It is speculated that nonrecoverable compression is caused by closure of the pore space liberated by transferring absorbed water to the benefit of bulk water porosity. Also, shrinking of the elastic domain (i.e., the region of elastic behavior) has been deduced to occur as a result of heating, dielectric coefficient decrease, or ionic concentration increase, independent of plastic yielding. In analogy to thermal softening, the three latter cases will be referred to as chemical softening. A single parameter, namely the accumulated mass transfer, is iden-
tized at controlling these changes. Because the mass transfer is reversible, the yield surface undergoes a reverse growth during cooling, rehydration, or when Δω < 0 (Fig. 13). Thus,

\[ f = f_0 e^\omega D = 0 \]

where \( e^\omega \) is the volumetric plastic strain.

When the shrinking yield surface reaches a constant stress point, the yield surface cannot shrink any more and compensation of the hardening role is used to describe plastic failure and plastic consolidation under chemical or thermal loading:

\[ f = \left( \frac{2\sigma_0}{\rho D(\gamma, \phi)} \right)^2 + \left( \frac{2q}{M0(\rho D(\gamma, \phi))} \right)^2 = 0 \]

where \( q \) is the principal stress difference, \( p^c \) is the apparent preconsolidation effective pressure, and \( M(0) \) is a variable slope of the critical-state line, depending on soil chemistry.

Thus, shear strength depends on mass transfer, which is a phenomenon of the nanoparticle size and shape of the nanoparticle or the number of molecular layers of adsorbed fluid at the nanoparticle contacts, as discussed in previous sections. Dependence of the yield-surface size on temperature has been determined experimentally by Hueneck and Baidul (1990). In what follows, the yield-surface size is written as depending on the total mass transfer \( D \), a function of the thermal and chemical history:

\[ p^c = p_0 e^\omega \exp \left( \frac{1}{\lambda} \ln \left( 1 - \omega D(1 + e_0)^{\phi} \right) \right) \]

where \( p_0 \) is the initial preconsolidation effective pressure; \( \lambda \) is the thermal, plastic bulk modulus; \( e_0 \) and \( e_0 \) are initial void ratio change to \( e_0 \) from a state at \( p/t_0 = 1 \); \( D_0 = p/t_0 \) is the total initial stress of the immobile water, \( \omega_0 \) is the ratio of the immobile water, \( \omega_0 \) and \( \omega_0 \) are constants.

The variable slope of the critical-state line \( M(0) \) corresponds to the observed increase in frictional strength with decreasing dielectric constant (Siddharth and Rao 1973). It should be noted that this increase is not substantial for \( D > 10 \). However, below that value the growth in strength is remarkable. This agrees with the observation of Israelachvili et al. (1988) on the variation of the critical shear stress at the nanoparticle contacts. An exponential variation of the coefficient \( M \) is thus assumed:

\[ M = M_0 e^\omega \exp \left( \frac{\omega_0}{\omega_0} \right) \]

where \( M_0 \) is the initial critical state line coefficient, and \( \omega_0 \) is a constant.

The plastic strain is defined through its rates, and in terms of its volumetric and deviatoric components \( \dot{e} \) is defined as

\[ \dot{e} = \dot{e}^p + \dot{e}^p \]

where \( g \) is plastic potential, and \( \Delta \) and \( \Delta \) are plastic multipliers, functions of rates of temperature, dielectric constant, ionic concentration, and valency. The former multiplier is obtained through usual procedure from Prager’s consistency equation, whereas the latter is an arbitrary function (Hueneck and Baross 1990).

The total strain rate (for brevity in matrix notation) is

\[ \dot{e} = \dot{e}^p + \dot{e}^p + A + M(0)C \]

where \( \dot{e}^p \) is tangential nonsymmetric elastoplastic matrix, \( A \) is a matrix of thermal and flocculation reversible expansion coefficients, \( M(0) \) is a stress-dependent matrix of irreversible thermochemical moduli, and \( C \) is the vector of environmental load variables.

The constitutive law for immobile water describes a dependence of its density on effective stress and temperature. As mentioned earlier, such a relationship may be determined directly from the Monte Carlo simulations presented by Slipper et al. (1991). In related work, Ma and Hueneck (1992) used the constitutive law for ordinary water at high densities corresponding to the density of adsorbed water.

The system of governing equations which has been developed in previous sections is complete and allows solution of boundary-value problems related to practical engineering questions. For example, Ma and Hueneck (1992) have solved the problem of infinitely long, decaying, line heat source in an elastic cylindrical clay mass using a partially implicit finite difference technique. The increase of pressure of bulk water around the heat source is substantially reduced, due to changes in permeability caused by the thermal degradation of adsorbed water. Permeability shows a local increase up to three orders of magnitude in the range of high temperatures.

Conclusions

Mixture theory for clays subjected to environmental (i.e., thermal and chemical) loads developed in this paper leads to a macroscopic model. The mechanisms and the variables describing them have clear origins in microscopic and molecular mechanics. Experiments and statistical mechanics compute calculations in recent years have given new understanding of the behavior of liquids in nanopores, particularly of water in dense clays. A new variable mass of transfer of adsorbed water due to thermal and chemical loads appears to play a central role in changes in permeability and development of elastic and plastic strains.

It is also clear that further conceptual, computational, and experimental studies should include not only investigation of effective porosity and changes in the volume of immobile fluid due to environmental loads, interactions between chemicals, water, clay and permeability variations, but also should include influence of the microscopic- and molecular-scale phenomena on macroscopic elastic and plastic behavior of the clay skeleton.


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