Water–mineral interaction in hygromechanics of clays exposed to environmental loads: a mixture-theory approach[1]

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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 denses 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 charge 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 : conductivité hydraulique, contrainte effective, charges environnementales, thermo-chimio-plasticité.

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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 nanopores ($<10^{-9}$ m) corresponding to the size of clay interstices has 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 strain, 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 Hulbert 1986; Stępkowska 1990) (Fig. 1). (1) Free or bulk water, which is able to flow due to hydraulic gradient at room temperature. (2) Intercluster 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) Intracluster 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 intracluster 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-

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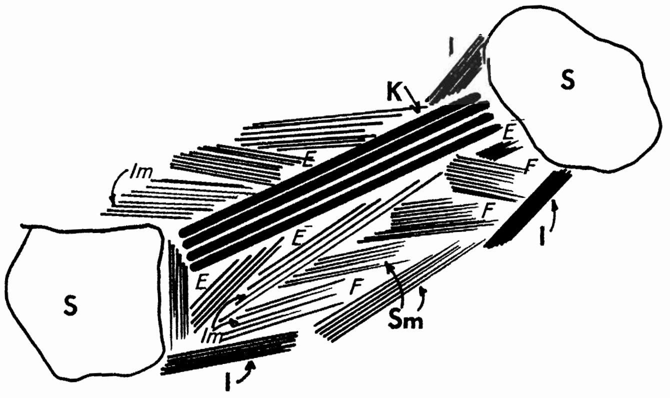

FIG. 1. Forms of water in high-density clay soil. F, free or bulk water; E, external or intercluster water; Im, interlamellar or intracluster water; S, silt; K, kaolinite; I, illite; Sm, smectite.

ardous wastes or accidental spills, may dramatically change solid–liquid interaction in clays. The effects of these loads are classically dealt with using the concept of diffuse double layer (DDL) which may form in polar liquids within sufficiently large single micropores and around mineral particles. The DDL theory derived from the Poisson–Boltzmann equation has been exhaustively discussed in the past (see e.g., Derjaguin–Landau–Varwey–Overbeek (DLVO) theory as presented in van Olphen (1977), Yong and Warkentin (1975), and Mitchell (1976)) and will not be dealt with here. However, most pores in the dense clays used for radioactive waste barriers are of the order of 6–50 Å (1 Å = 0.1 nm) (Pusch and Hökmark 1990). Recent experiments in surface physics and molecular dynamics simulations indicate that in the interstices smaller than 30–50 Å there is no room for development of such a continuum field like DDL (Israelachvili 1985). No particular alternative microstructural theory has been proposed until now for such interstices, and all numerical results are being obtained through massive computer simulations. Thus, phenomenological approaches to describe properties of this water are still the only solution for engineering purposes.

This paper presents such a phenomenological approach to saturated clays within the framework of the theory of interacting mixtures. Mixture theory was developed for gaseous and liquid chemical mixtures by Fick (1855) and Stefan (1871) and extended for mixtures of liquids and deformable solids by Truesdell *et al.* (1969, 1986). Finally, the mixture theories addressing porous and (or) granular solids or directly soils were developed by Passman *et al.* (1986), Raats (1986), Morland (1972), Hueckel (1987), Hueckel and Ma (1991), and Ma and Hueckel (1991). It should be added, finally, that parallel to mixture theories, thermohydromechanical theory (Biot 1941) used in geophysics and petroleum engineering and thermochemical theory (Low 1979) used in agrosciences apply to clays as well.

One of the principal assumptions of mixture theory is that any element of the mixture is simultaneously occupied by superimposed elements of the constituents (Fick 1855; Stefan 1871). Thus, there is no need for a definition of a physical boundary between the constituents, nor for conditions of interaction between them along such a boundary. Rather, the interaction between the constituents is attributed to the entire element of the mixture. As a principle, it is assumed that to determine the behavior of the mixture it is sufficient to know the properties of the constituents and their possible interaction. For clays, the mixture may, moreover, be assumed as binary (i.e., with an equal temperature in all constituents). This is based on the fact that heat convection in clays is negligible in comparison with conduction (Beastle and Mittempergher 1980; Heremans *et al.* 1980).

In what follows, first the mixture constituents will be defined, then four basic components of the mixture theory will be dealt with for each constituent. These are mass-conservation laws together with a mass-transfer equation, linear momentum balance with the effective stress concepts for clays, and energy-conservation laws. Finally, constitutive laws for the constituents will be presented. In particular, a novel chemoplasticity for clays will be presented. The constitutive properties are assumed to depend on variables pertaining to a given constituent only, according to the principle of phase separation developed for multiphase flow theory by Drew and Segel (1971) (see also Nunziato and Passman 1981). This is different from the equipresence 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

Gas 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 in the natural conditions, a part of the adsorbed water is not able to flow and thus will be referred to as immobile water (Kemper *et al.* 1964).

Further considerations are restricted to high-density clays, such as those used in radioactive barriers, for which bulk density exceeds 1.8 Mg/m^3. This limitation is very important because it excludes from consideration clay suspensions, gels, 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 interlamellar spaces. Only a minor fraction of the water is located around the external surfaces of clusters of nearly parallel platelets and in the voids between them. For an artificial Na montmorillonite, Pusch and Hökmark (1990) estimate that at saturation and a bulk density of 1.80 Mg/m^3, more than 60% of the water is immobile. For natural Boom clay (nominally with 22% smectite, 19% illite, 29% kaolinite, and 30% quartz) at a total water content of 13%, the ratio of interlamellar to total water content has been calculated to be 24, 37, and 49%, respectively, for two, three, and four monomolecular layers of interlamellar water (Baldi *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 regarded in 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 fractions n_s and n_f of solids and fluid, respectively, are defined as

$$\begin{aligned} & n_f = n_2 \\ [1] \quad & n_s = n_c + n_1 \\ & n_s + n_f = 1 \end{aligned}$$

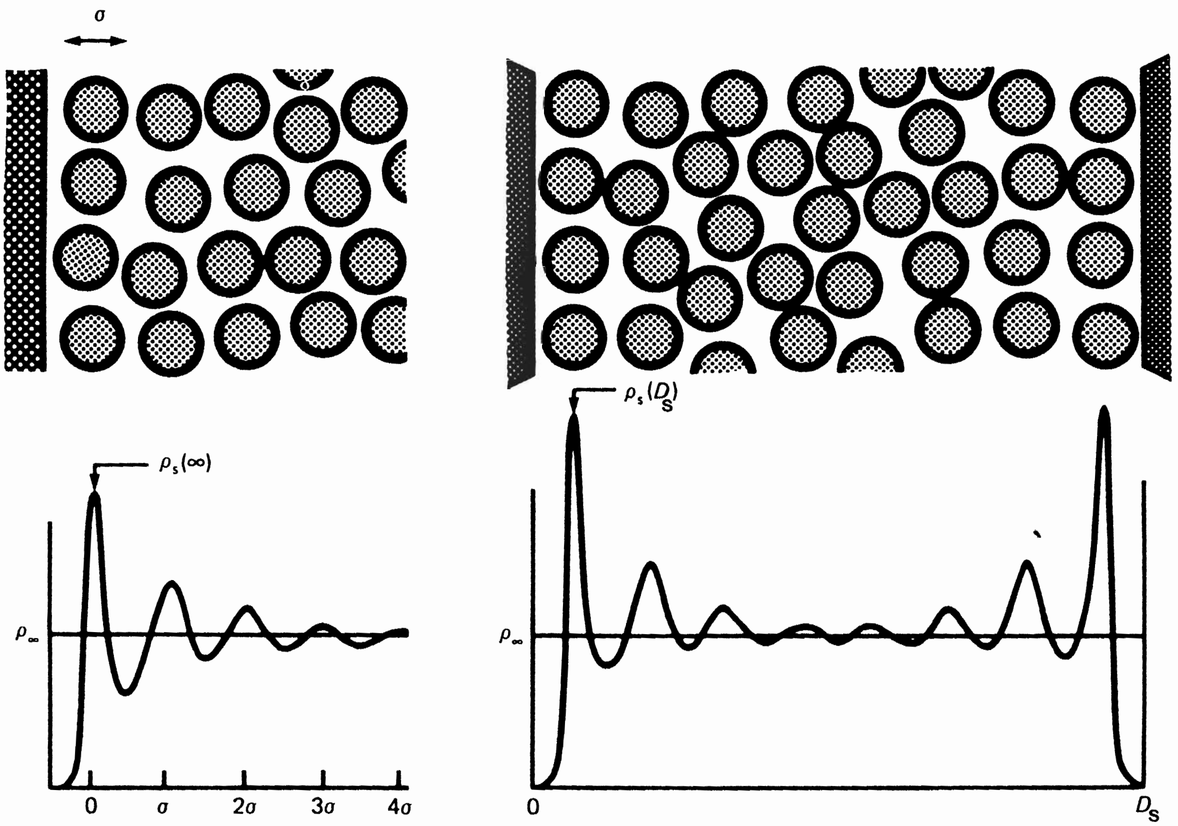

FIG. 2. Liquid molecular arrangement and profile of density ρ_s in a pore with infinitely distant walls ($\rho(\infty)$) and in a nanopore with the opening size D_s ($\rho_s(D_s)$) (after Israelachvili 1975).

where n_1 and n_2 are volume fractions (or porosities) of immobile and mobile water, respectively; and n_c is the volume fraction of the clay mineral:

$$[2] \quad n_1 = \frac{V^i}{V}, \qquad n_2 = \frac{V^m}{V}, \qquad n_c = \frac{V^c}{V}$$

where V^i and V^m are the volumes of immobile and mobile water, respectively; V^c 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 ρ^f and ρ^s are defined for fluid and solid constituents, respectively, as follows:

$$[3] \quad \rho^f = n_2\gamma_{w2}, \qquad \rho^s = n_c\gamma_c + n_1\gamma_{w1}$$

where γ_{w1}, γ_{w2}, and γ_c are specific densities of immobile and mobile water and clay mineral, respectively.

To take into consideration changes in adsorbed water, the mass-transfer approach has been developed (Hueckel 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 (Hueckel 1988; Hueckel and Ma 1991).

From this assumption it follows that solid and fluid volume fractions n_s and n_f 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 densities in [3] are 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 their particles. In practice, there are no means to determine this difference from a macroscopic experiment. What is determined commonly as 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 interstices (50 Å) loses its special structure. However, experiments by Pusch (1987) and Pusch and Güven (1989) suggest that in clays this process continues through 150 up to 250°C (see also Grim 1968 and Kezdi 1975, p. 47). Thus for present purposes, the classical soil mechanics method for measuring water content is inconclusive. Heating to a higher temperature can yield the total volume of water, but the fraction of mobile water still remains undetermined.

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 DDL describes accurately the behavior of adsorbed water only at (*i*) interparticle distances greater than 50 Å, and (*ii*) low salt concentrations,

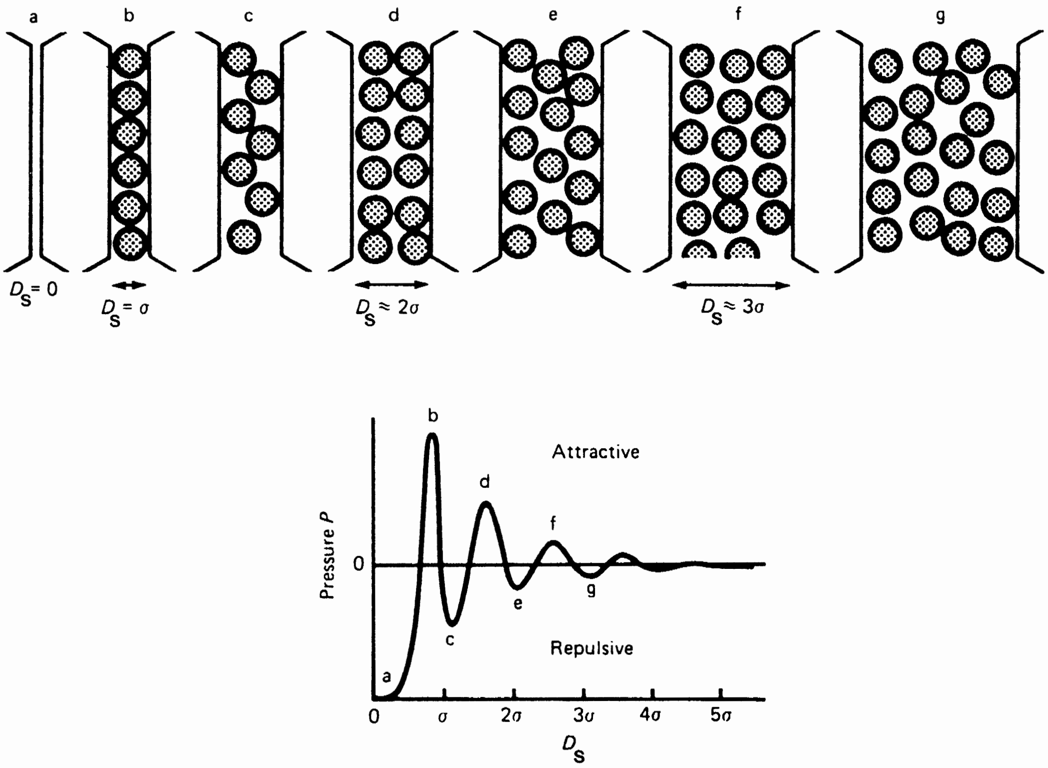

FIG. 3. Molecular arrangement (schematic) and solvation pressure in nanopores as a function of platelets separation D_s, to be possibly superimposed on a double layer type pressure, monotonically decreasing with distance (from Israelachvili 1975).

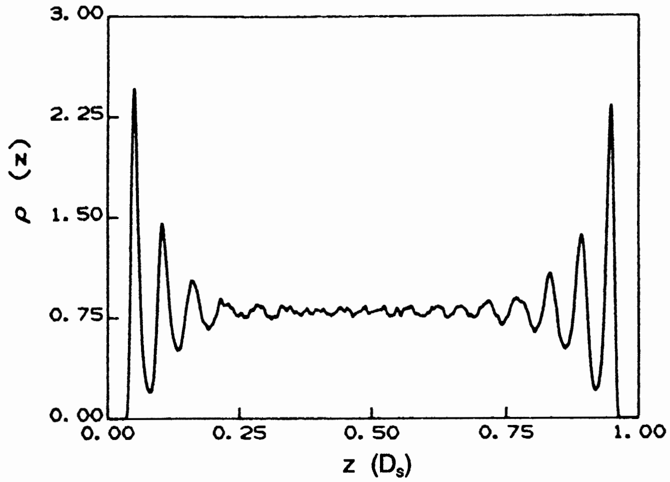

FIG. 4. Liquid density (ρ) profile across a slit-pore 16.5 liquid molecule diameters large as a function of the distance normalized with respect to pore width z/D_s (Monte Carlo simulation) (from Schoen *et al.* 1987).

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, cation-cation, water-clay, cation-clay, 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 14.2-Å Na smectite, the cations were binding to the clay surface and the average interlayer water density obtained

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[2] N.T. Skipper, K. Refson, and J.D.C. McConnell. Monte Carlo simulations of Mg- and Na-smectics. In preparation.

by Skipper *et al.* (footnote 2) was 1.14 ± 0.04 g/cm^3. In 14.7-Å Mg smectite, the structure of the interlayer water was heavily dominated by the centrally located cation. The average density of the interlayer water in Mg smectite was found as 1.38 ± 0.04 g/cm^3. 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 immobile water. In contrast, for Na montmorillonite with water contents higher than 78%, Anderson and Low (1958) and Low (1979) found the adsorbed water to be less dense than bulk water (see also Martin 1962).

Early experiments performed by Kemper *et al.* (1964) to evaluate the mobility of adsorbed water as opposed to bulk water indicate that at least two molecular layers at 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 forming 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-third of the corresponding value for bulk water. Earlier tests on Na montmorillonite by Adams *et al.* (1979) and tests by Pusch and Carlsson (1985) and Carlsson (1985) have also shown lower diffusivity of clay water.

In conclusion, in interstices larger than about 10 molecular diameters, there is a number (two to four) of molecular layers which have highly different flow properties from bulk liquid. In interstices smaller than 7–10 molecular diameters, the flow 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 Truesdell 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

$$[4] \quad \frac{D^s\rho^s}{Dt} + \rho^s v^s_{i,i} = \dot{\mu}^s$$

$$[5] \quad \frac{D^f\rho^f}{Dt} + \rho^f v^f_{i,i} = \dot{\mu}^f$$

where D()/Dt is the material time derivative and comma is spatial derivative, and v_i^f and v_i^s are velocity components of fluid and solid elements, respectively. The variables $\dot{\mu}^s$ and $\dot{\mu}^f$ are rates of mass transfer toward solid and fluid phases, respectively, interrelated through Truesdell's (1969) axiom

$$[6] \quad \dot{\mu}^f + \dot{\mu}^s = 0$$

Equation [6] assumes that no mass can be generated in one constituent through any process, without an equal mass loss in the other constituent. Standard equation of mass conservation for the whole medium also applies. Mass transfer is a central feature in the analysis of the effects of environmental loadings.

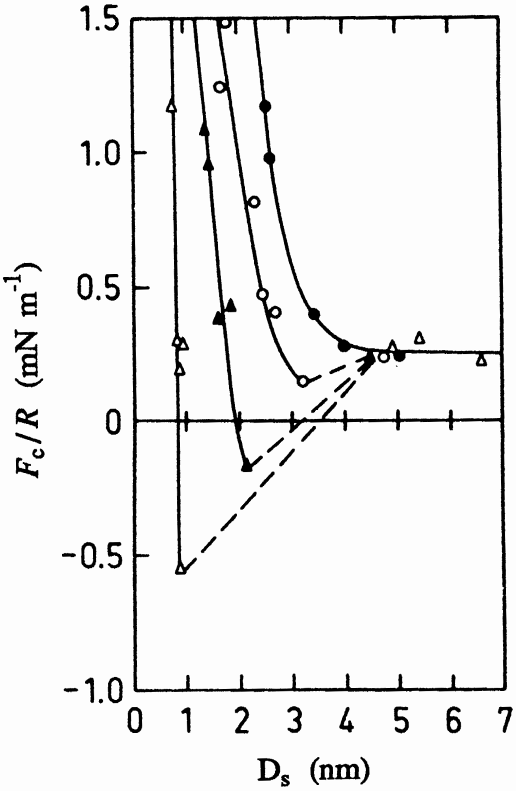

FIG. 5. Decrease of short-range force F_c vs. separation D_s for different temperatures. The force is normalized *w/r* to surface curvature radius R (from Claesson *et al.* 1986). ●, 15°C; ○, 20°C; ▲, 30°C; △, 37°C.

In classical approach, such as three-dimensional consolidation theory, [4] 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 may be reached in mixture theory (Ma and Hueckel 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 waters 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 solid 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. Thus, 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 n_2. Therefore,

$$[7] \quad q_i = n_2(v_i^f - v_i^s)$$

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

$$[8] \quad \frac{D^f(n_2\gamma_{w2})}{Dt} + n_2\gamma_{w2}v^s_{i,i} + (\gamma_{w2}q_i)_{,i} = \dot{\mu}^f$$

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[3] K. Refson, N.T. Skipper, and J.D.C. McConnell. Molecular dynamics simulation of water mobility in smectics. In preparation.

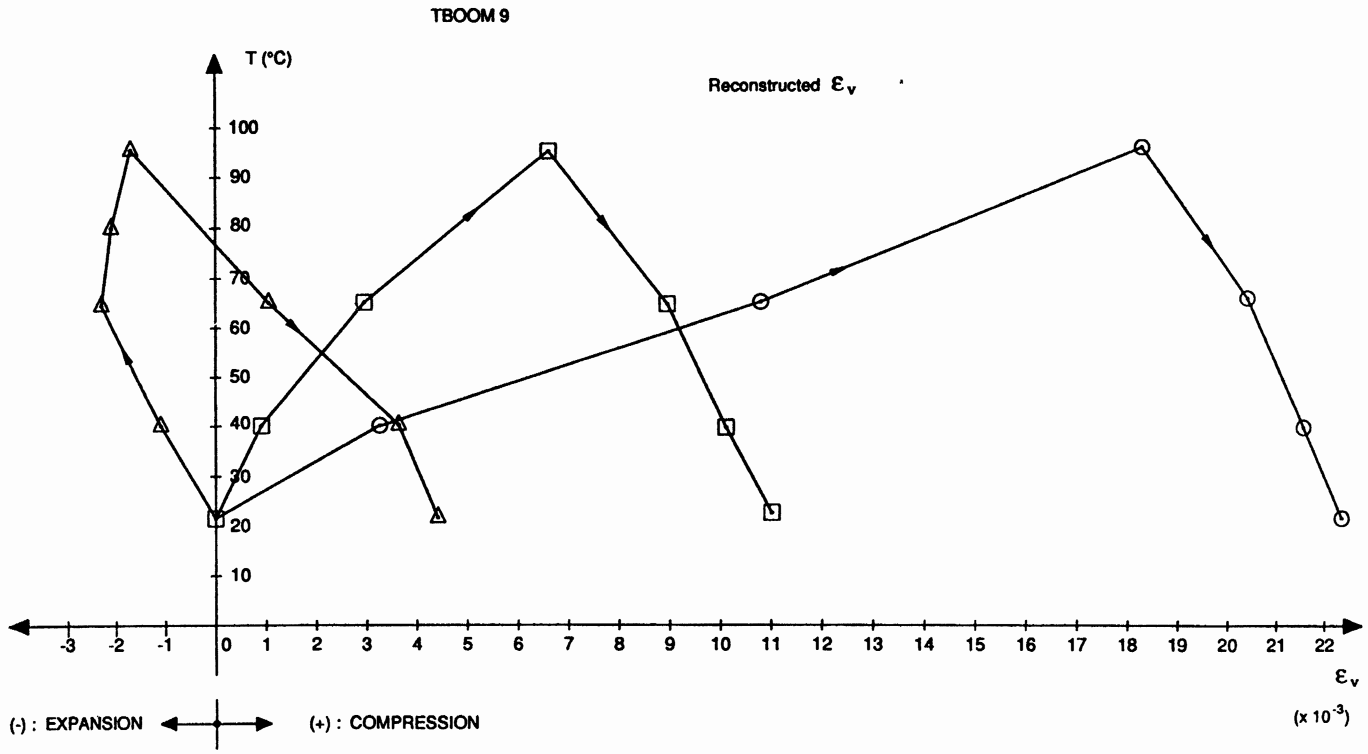

FIG. 6. Thermal volumetric strain (ϵ_v) for different mean stresses for Boom clay (from Baldi *et al.* 1990). △, $p' = 1$ MPa; □, $p' = 3$ MPa; ○, $p' = 6$ MPa.

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 $\rho = \rho^f + \rho^s$, 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.

Sensibility 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 Güven (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 seals 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 reportedly obtained in the laboratory (Khitarov and Pugin 1966). As smectite is altered to illite, the intracluster water becomes free water, with the consequent changes in water density (Powers 1967; and Burst 1969; Winterkorn and Baver 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 Churaev 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 switchover 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 Esrig 1969; see also Mitchell 1975). According to the thermoplasticity 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 (Tidfors and Sallfors 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 than could be expected simply from the thermal change in water viscosity (see also Mitchell 1975; Ma and Hueckel 1992). Preliminary studies with molecular dynamics were performed for montmorillonite (Refson *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 molecules, leading to this increasing diffusivity. A model of diffusion 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 presence of some residual interlayer water (Grim 1968). Heating-induced consolidation was also observed in illite (Paaswell 1967; Campanella and Mitchell 1968; Plum and Esrig 1969; Houston and Lin 1987; Baldi *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 (Grim 1968). However, in a heating experiment, Pontida clay with 20% kaolinite and 25% illite has shown thermal consolidation (Baldi *et al.* 1988). Campanella and Mitchell (1968) have also shown that kaolinite consolidates thermally.

Chemical loading

Olson and Mesri (1970) and Sridharan and Venkatappa 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 smectites, much less so in illites, and almost not at all in kaolinites. Sridharan and Venkatappa 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 montmorillonites 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*) concentration of the electrolyte in the free pore fluid (Olson and Mesri 1970).

As far as shear strength is concerned, no significant effect was found at decreasing electrolyte concentrations in kaolinites and montmorillonites. However, a distinct strength decrease was caused in sodium illite. Increases in cation valence invariably increase strength (Olson 1974). Presumably, a well-developed DDL reduces the friction at contacts between strong clusters in illite. Low strength and the lack of any effect of concentration changes in sodium montmorillonite were attributed to the low mechanical strength of the flakey particles themselves. The effect of a change in pore fluid on strength was investigated by Sridharan and Venkatappa Rao (1973). The shear box strengths in terms of friction angle and cohesion intercept were all increasing with decreasing dielectric constant. The effect was remarkable at dielectric constants less than 5. Kaolinite appears to be more sensitive to dielectric constant drop than montmorillonite. 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. However, it should be noted that all the above experiments were performed on clays at initial void ratios between 2 and 4.

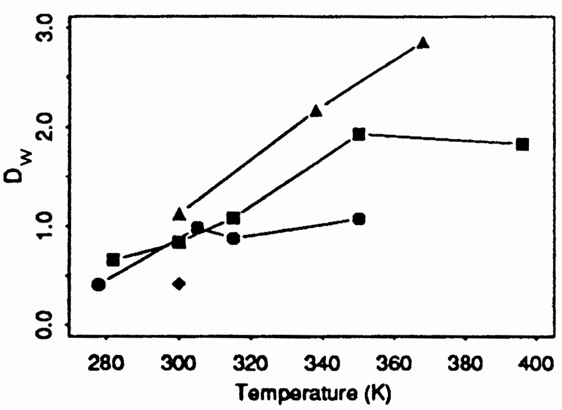

FIG. 7. Computed (■, Mg smectite; ●, Na smectite) and experimental (▲ and ◆, respectively) values of diffusion constant D_w for clay water as a function of temperature (from Refson *et al.*, see footnote 3).

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 cracking (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-wall permeameter (Anderson *et al.* 1985). However, at a compressive stress applied in a flexible-wall permeameter, 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*) chlorite or kaolinite causes, respectively, a 660- and 7.5-fold growth of hydraulic conductivity in the absence of external stress, and conversely a 500- and 0.02-fold drop under a moderate stress, (Bowders and Daniels 1987). Mitchell and Madsen (1987) gave a thorough review of various effects of inorganic and organic chemicals on clay hydraulic conductivity as applied generally to liners. Inorganics, when they increase concentration and cation valence, cause flocculation and reduce swelling, leading to an increase in hydraulic conductivity. Organics, more important from the point of view of the human environment, are the focus of concern. They may affect clays through a variety of adsorption, intercalation, and cationic-exchange mechanisms. Permeation by a series of a sequentially miscible organic fluids may produce much larger increases in hydraulic conductivity than a casual order of permeation (Fernandez and Quigley 1985). The interlamellar spaces in montmorillonite are not always accessible to guest fluids, depending on the molecular size and electrochemical properties (Sawhney *et al.* 1990; Yong and Rao 1990). Thus often only external immobile water may be subjected to removal.

One of the important properties of liquid–solid interaction in clays affected by chemicals is chemically induced shrinkage cracking. This phenomenon occurs often along weakness planes created during clay compaction or other mechanical actions and sometimes becomes a primary cause of a breakthrough flow (e.g., see Mitchell and Madsen 1987; Fernandez and Quigley 1988; Storey and Peirce 1989). Possible triggering mechanisms are cracking originated through compaction techniques at the grain boundaries, or flocculation, which constitute a local soft inhomogeneity initiating a crack propagation (Storey and Peirce 1989). Recent studies indicate a critical role of effective stresses in chemical damage and maintaining desired hydraulic conductivity in clay barriers exposed to organics (Fernandez and Quigley 1991). In particular, whether the effective stress is added before or after the damage appears important.

Most of the processes that have been discussed in this section are believed to be reversible, with the notable exception of shrinkage cracking.

Mass-transfer equations

The behavior that has just been described prompts the hypothesis that changes in volume and hydraulic conductivity caused by environmental loads result from changes in volume of a part of the external adsorbed and (or) interlamellar water. Because of the definitions of constituents adopted earlier, such removals and readsorptions of the adsorbed water may be idealized as mass transfers from solid phase to liquid phase and vice versa (Hueckel 1988; Hueckel and Ma 1991; Ma and Hueckel 1991). The following section considers only reversible mass transfer. Since such mass transfer involves only immobile water, it will be a function of the volume fraction of the immobile water n_1. Because of the restriction [6], only the mass transfer of one constituent needs to be defined. Furthermore, although it may be expected that a combination of temperature and chemical loads can affect the mass transfer differently from the separate action of these loads, no data exist to justify any such coupled equation.

The mass-transfer rate (per unit volume) for solid due to temperature increase only is therefore assumed to be a linear function of the temperature rate:

$$[9] \quad \dot{\mu}^{\mathrm{s}}_{T} = \frac{\dot{T}\rho^{\mathrm{f}}}{T_{\mathrm{d}} - T_{\mathrm{i}}}\,(n_1^0 - \rho^{\mathrm{s}} S_{\mathrm{s}} i\delta) \qquad T_{\mathrm{i}} \le T \le T_{\mathrm{d}}$$

where T_{i} and T_{d} are, respectively, temperatures at the onset of water structural change and at the termination of immobile water degradation (possibly about 150°C); n_1^0 is the initial value of immobile water porosity; S_{s} is the total specific surface area; and i and δ are the number and the thickness, respectively, of molecular layers of water (2.58 Å), which are believed to remain at T_{d} (Burst 1969; Pusch and Hökmark 1990).

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 interlamellar 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 Madsen 1987; Fernandez and Quigley 1985, 1987; Yong and Rao 1991; Sawhney *et al.* 1990; Budhu *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 (Budhu *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:

$$[10] \quad \dot{\mu}^{\mathrm{s}}_{\mathrm{D}} = \frac{-\dot{D}\rho^{\mathrm{f}}}{D^{\mathrm{w}}(T)}\,(n_1^{0\mathrm{a}} - \rho^{\mathrm{s}} S^{\mathrm{a}}_{\mathrm{s}} i\delta) \qquad D \le D^{\mathrm{w}},\ \dot{T} = 0$$

where D^{w} and D are dielectric coefficients, respectively, of water and of the fluid mixture currently permeating clay, defined as $D = cD^{\mathrm{g}} + (1 - c)D^{\mathrm{w}}$, where c and D^{g} are, respectively, the permeant concentration and the dielectric constant of the guest liquid; the integer number i is the number of irremovable layers of adsorbed water from the mineral wall; $S^{\mathrm{a}}_{\mathrm{s}}$ is the specific surface area available for the molecules of the guest liquid; and $n_1^{0\mathrm{a}}$ 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 α, the balance reads

$$[11] \quad \sigma^{\alpha}_{ij,j} + p^{\alpha}_{i} + \rho^{\alpha} g_i - \rho^{\alpha}\frac{\mathrm{D}^{\alpha} v^{\alpha}_{i}}{\mathrm{D}t} = 0$$

where σ_{ij} is the stress component, g_i is the gravity component, and p_i is the interaction force component.

The interaction forces are then postulated to be the sum of a term proportional to water specific discharge q_i, a term dependent on effective porosity and bulk water pressure gradients and a term proportional to the interconstituent mass-transfer rate (following Bowen 1975; Truesdell and Toupin 1960; Raats 1986). Assuming that area fractions are space invariant,

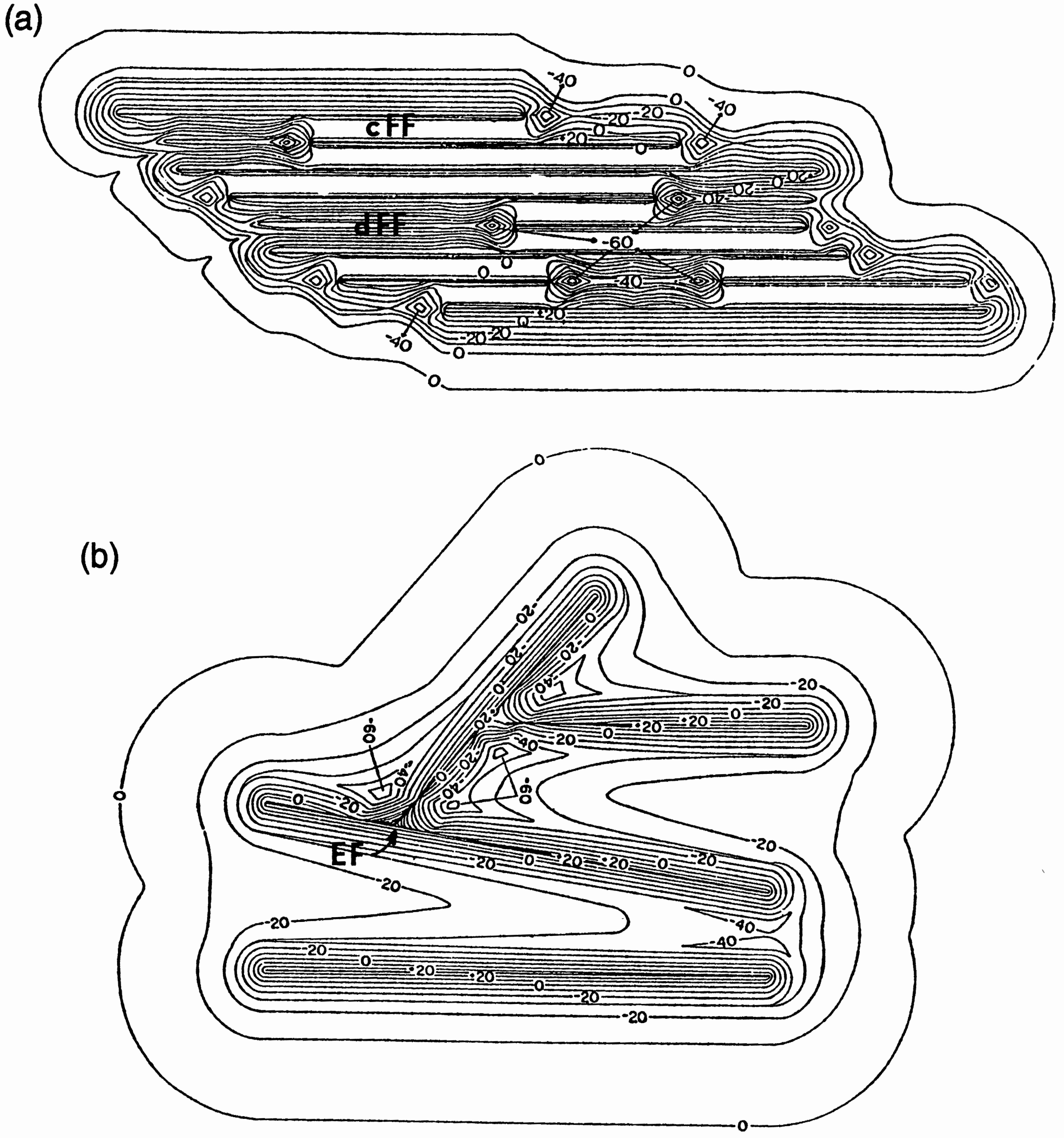

FIG. 8. (*a*) Close face-to-face (cFF) and distant face-to-face (dFF) contacts in montmorillonite. (*b*) Edge-to-face (EF) contact in kaolinite (with energy equipotential lines around clay particles from Bennett and Hulbert 1986).

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 during shear 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 expected in a Newtonian viscous fluid. The shear viscosity in such small interstices (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

$$[12] \quad p_i^{\mathrm{f}} = \frac{n_2 \nu_{\mathrm{d}}}{k} q_i - \dot{\mu}^{\mathrm{f}} B_i^{\mathrm{f}} + n_2 u_{,i} - (n_2 u)_{,i}$$

$$[13] \quad B_i^{\mathrm{f}} = v_i^{\mathrm{f}} - v_i \qquad v_i = \frac{1}{\rho} \Sigma\, \rho^{\alpha} v_i^{\alpha}$$

where $\nu_{\mathrm{d}}(T)$ is dynamic viscosity of the fluid, and B_i^{f} and v_i are diffusion velocity and mean velocity of the mixture, respectively. Thus, the linear momentum balance equation for fluid [11] reduces to the following:

$$[14] \quad q_i = -\frac{k}{\nu_{\mathrm{d}}} [(u)_{,i} + \rho^{\mathrm{f}} g_i]$$

Thus Darcy's law is recovered.

Permeability

Permeability of nonfractured, dense clays is connected, 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_2 (Olsen 1962). The relationship between the two variables is given as

$$[15] \quad k = \frac{1}{\pi T_{\mathrm{r}}^2 S_{\mathrm{sm}}^2} \frac{(n_2)^3}{(1 - n_2)^2}$$

where S_{sm} is the specific surface area relative to the mobile water space; π is a shape factor, usually taken as equal to 2.5; and T_{r} is tortuosity factor, usually taken as 1.414. The mobile water porosity n_2 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 interstices produced by stress or temperature changes. Cheung *et al.* (1987) evaluating n_2 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 convenient to use a reference permeability value k_0 determined in an undeformed configuration, characterized by an initial value of bulk water porosity n_2^0:

$$[16] \quad k = k_0 \left(\frac{n_2}{n_2^0} \right)^3$$

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 1961). Thus, in considering the partial stress in the bulk water, the customary definition will be adopted (see Bazant and Krizek 1975; Kowalski 1983) 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_2 is used as the scaling factor, and so

$$[17] \quad \sigma^{\mathrm{f}} = n_2 u, \qquad \sigma^{\mathrm{s}} = \sigma' + (1 + n_2) u$$

where σ^{f}, σ^{s}, σ', and σ are, respectively, the partial isotropic stresses in the fluid and the solid, 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 familar Terzaghi's (1925) effective stress principle is recovered:

$$[18] \quad \begin{aligned} \sigma &= \sigma^{\mathrm{s}} + \sigma^{\mathrm{f}} \\ &= \sigma' + u \end{aligned}$$

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 (1961) 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 controversy 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 a 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 σ' 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 mechanistic stress–strain models that may be derived for saturated clay from various effective-stress definitions following, respectively, (*i*) Lambe (1960) and Mitchell (1962) (Fig. 9*a*); (*ii*) Sridharan (1968), Sridharan and Rao (1973), Balasubramonian (1972), and Morgenstern and Balasubramonian (1980) (Fig. 9*b*); and (*iii*) Bolt (1956), Lambe (1969), Nagaraj and Jayadeva (1981), and Graham *et al.* (1989) (Fig. 9*c*). In these models the interparticle contact stress σ_{c}, and the net repulsive less attractive force $R - A$ are connected in series or parallel in two different arrangements, being in addition set in parallel with the bulk water pressure u.

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. 9*c*) 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 Resendiz (1965). The series model incorporates the Terzaghi's principle and additionally a physicochemically 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 (1992). 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.

Constitutive laws

In this section, mechanical properties of the immobile liquid are first discussed in view of some recent results of studies on the behavior of fluid in nanopores. In particular, a dependence of the shear behavior of interparticle contacts on molecular properties of interlamellar liquid is shown to lead to a novel chemo-thermo-plastic constitutive equation.

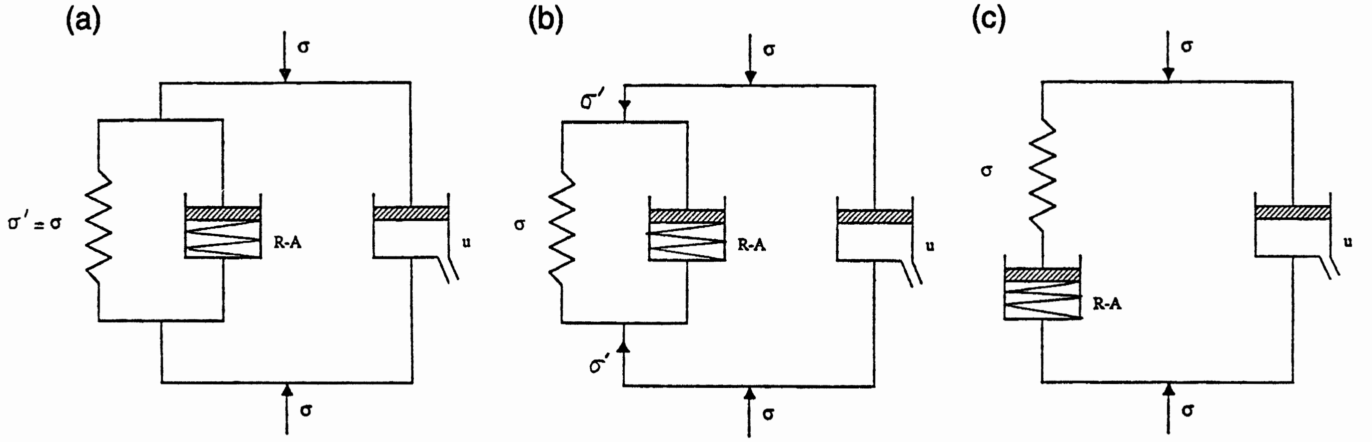

FIG. 9. Mechanistic models for effective stress σ'. (*a*) Parallel connection. $R - A$ forces do not contribute to σ'. (*b*) Parallel connection. $R - A$ forces contribute to σ'. (*c*) Series connection.

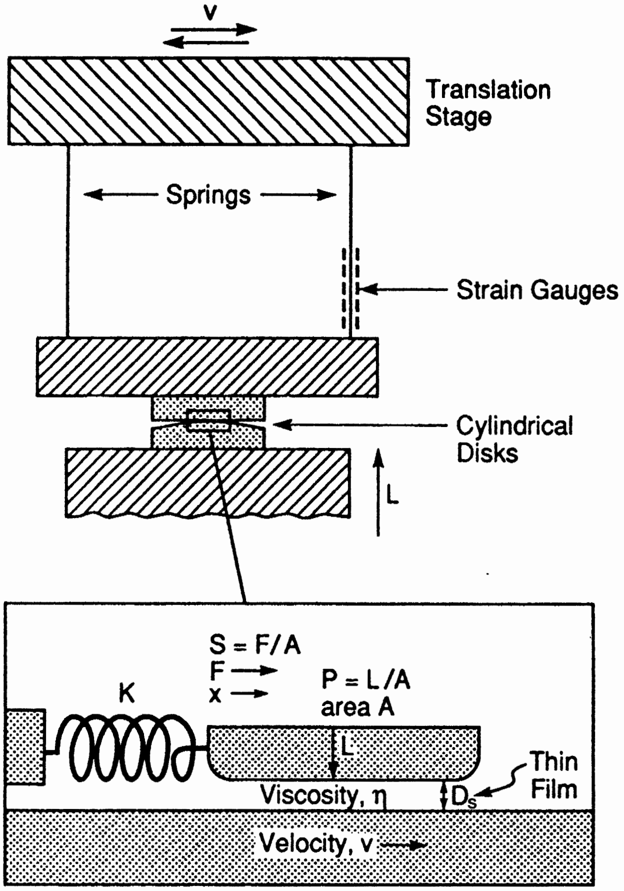

FIG. 10. Intermolecular shear apparatus (from Gee *et al.* 1990). *F* is shear force, *L* is normal force, and *A* is contact area.

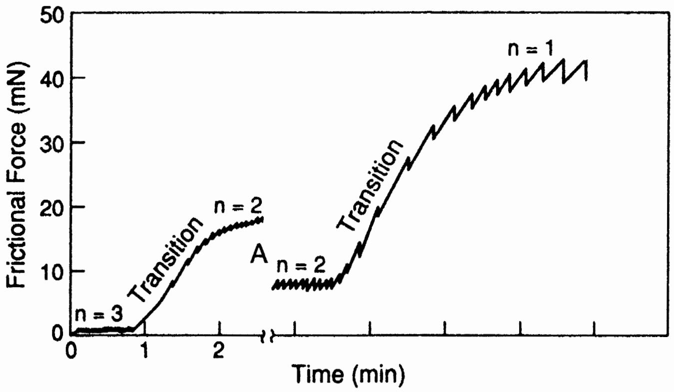

FIG. 11. Shear force during interlayer transition for a model liquid. The jump at A is due to technical factors, viz. change in the contact area (from Gee *et al.* 1990). *n*, number of molecular layers.

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; Cushman 1990) (Fig. 12). However, as opposed to the experimental studies outlined earlier, the numerical simulations showed that shear stresses would abruptly decreasse 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_c) due to the (internal) adhesion force between the two surfaces and another part due to the externally applied load:

$$[19] \quad \tau^* = S_c + C\sigma^*$$

where τ^* and σ^* are the total shear and normal stresses, respectivley, at the contact (at the particle scale). The most important conclusion is that the S_c 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 2×10^7 N/m^2.

It should be emphasized that only some of the results quoted were obtained for water. Therefore their application

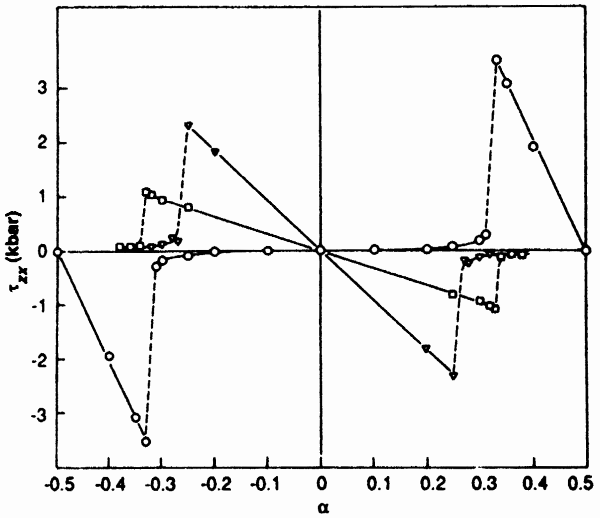

FIG. 12. Statistical mechanics simulation of the intermolecular shear stress in liquids at close separations as a function of tangential strain α. For separations: ○, 2.2σ; ▿, 3.1σ; □, 4.9σ. σ, molecular diameter. The first plot is shifted in phase over 0.5 (from Cushman 1990).

to all phenomena in clays may not be appropriate. However, simulations and experiments have shown that several properties of clay water are the same as those of other liquids in nanopores. It therefore may be concluded that a phenomenological shear failure condition should be used in which the properties of interlamellar liquid are taken into account, in addition to normal stresses or effective stresses in the skeleton.

It is also interesting to find that the shear strength for the thinnest liquid layers is independent of the velocity of motion of the liquid separating the surfaces (Israelachvili *et al.* 1988; Granick 1991). This means that the liquid in such contact behaves not as a viscous fluid but rather as a plastic granular material. Thus, if viscoelastic or viscoplastic (time-dependent) behavior is observed at a macroscopical scale in dense clays, it is to be attributed to a time-dependent, very slow seepage of the interlamellar water between pores, rather than to viscosity of the adsorbed water. Such time-dependent deformation related to flow of interlamellar fluid has been recently thoroughly discussed by Barbour and Fredlund (1989) in the context of "osmotically induced consolidation" resulting from ionic concentration gradients. This can be contrasted with "osmotic consolidation" caused by ionic concentration rate, which is discussed below.

Macroscopic constitutive laws

The thermo-elasto-plastic model for clays proposed earlier by Hueckel and Borsetto (1990) and Hueckel and Baldi (1990) is now extended to include chemical effects. This allows us to jointly treat temperature, stress, and chemical loads in their interaction to generate strain. The essential novelty of this model is that it includes as a variable the total accumulated mass transfer Ω of adsorbed water due to environmental loads, defined as a time integral over the whole history of the mass-transfer rate (see also Hueckel and Ma 1991):

$$[20] \quad \Omega = \int \dot{\mu}(\dot{T},\dot{D},\dot{c}_i)\,dt$$

where c_i is the ionic concentration in the bulk fluid.

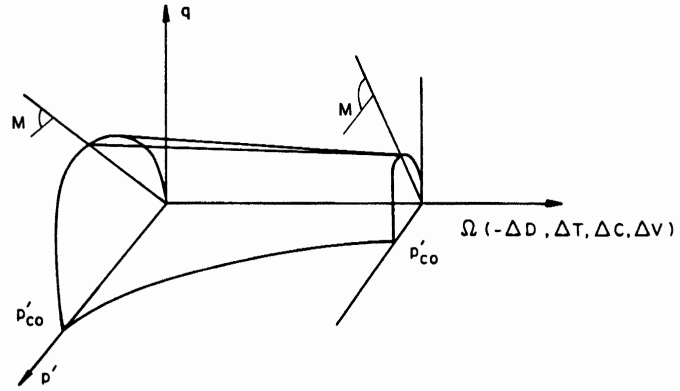

FIG. 13. Thermal and (or) chemical softening of the elastic domain for modified Cam-clay model. For symbols, see [23] and [24].

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. 9*c*. This stress will still be called effective stress σ'_{ij}. 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:

$$[21] \quad \epsilon_v^e = \frac{1}{\kappa(\Omega)}\sigma' - \alpha(\sigma')\Delta T + \beta\Delta D + \gamma\Delta c_i + \ldots$$

where $\kappa(\Omega)$ is the elastic bulk modulus depending on the total accumulated mass transfer; and α, β, and γ 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 in 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; Hueckel and Baldi 1990), (*ii*) an increase in ionic concentration or valence (e.g., Olson and Mesri 1970; Barbour and Fredlund 1989); or (*iii*) a decrease in dielectric constant (e.g., Sridharan and Venkatappa 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 identified as controlling these changes. Because the mass transfer is reversible, the yield surface undergoes a reverse growth during cooling, rehydration, or when $\Delta c_i < 0$ (Fig. 13). Thus,

$$[22] \quad f = f(\sigma'_{ij}, \epsilon_v^{pl}, \Omega) = 0$$

where ϵ_v^{pl} is the volumetric plastic strain.

When the shrinking yield surface reaches a constant stress point, the yield surface cannot shrink any more and compensatory plastic strain rates must develop. This produces plastic strain hardening to offset chemical or thermal softening. The following section uses a modified Cam-clay yield surface, and strain-hardening rule is used to describe jointly plastic failure and plastic consolidation under chemical or thermal loading:

$$[23] \quad f = \left(\frac{2\sigma'}{p'_c(\Omega, \epsilon_v^{pl})} - 1\right)^2 + \left(\frac{2q}{M(\Omega)\ p'_c(\Omega, \epsilon_v^{pl})}\right)^2 = 0$$

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

Thus, shear strength depends on mass transfer, which is a phenomenological counterpart of the change in the number of molecular layers of adsorbed fluid at interparticle contacts, as discussed in previous sections. Dependence of the yield-surface size on temperature has been determined experimentally by Hueckel and Baldi (1990). In what follows, the yield-surface size is written as depending on the total mass transfer Ω, a function of the thermal and chemical history:

$$[24] \quad p'_c = p'_{co} \exp\left\{\frac{1}{\lambda - \kappa(\Omega)}\left[e_{op} + (1 - a_o\Omega)(1 + e_0)\epsilon_v^{pl}\right]\right\} \left[1 - a_1 \frac{\Omega}{\Omega_a} - a_2 \left(\frac{\Omega}{\Omega_a}\right)^2\right]$$

where p'_{co} is the initial preconsolidation effective pressure; λ is the isothermal, plastic bulk modulus; e_0 and e_{op} are initial void ratio change to e_0 from a state at $p'_c/p_{co} = 1$; $\Omega_a = \rho^f n_{10}$ is the total initial mass of the immobile water, γ_{wi} is density of the immobile water; a_0, a_1, and a_2 are constants. The variable slope of the critical-state line ($M(\Omega)$ corresponds to the observed increases in frictional strength with decreasing dielectric constant (Sridharan 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 nanopore contacts. An exponential variation of the coefficient M is thus assumed:

$$[25] \quad M = M_0 \exp\left(\frac{\Omega}{\Omega_0}\right)$$

where M_0 is the initial critical state line coefficient, and Ω_0 is a constant.

The plastic strain is defined through its rates, and in terms of its volumetric and deviatoric components it is defined as

$$[26] \quad \dot{\epsilon}_v^{pl} = \Lambda_v \frac{\partial g}{\partial p'}, \qquad \dot{\epsilon}_q^{pl} = \Lambda_q \frac{\partial g}{\partial q}$$

where g is plastic potential, and Λ_v and Λ_q 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 (Hueckel and Borsetto 1990).

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

$$[27] \quad \dot{\boldsymbol{\epsilon}} = \boldsymbol{E}^{ep}\dot{\boldsymbol{\sigma}}' + [\boldsymbol{A} + \boldsymbol{M}]\dot{\boldsymbol{C}}, \qquad \boldsymbol{C}^T = [T, -D, c]$$

where $\boldsymbol{E}^{ep}$ is tangential nonsymmetric elastoplastic matrix, $\boldsymbol{A}$ is a matrix of thermal and flocculation reversible expansion coefficients, $\boldsymbol{M}$ is a stress-dependent matrix of irreversible thermochemical moduli, and $\boldsymbol{C}$ 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 Skipper *et al.* (1991). In related work, Ma and Hueckel (1992) used the constitutive law for ordinary water at high densities corresponding to the density of absorbed 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 Hueckel (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 computer calculations in recent years have given new understanding of the behavior of liquids in nanopores, particularly of water in dense clays. A new variable of mass transfers 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, and 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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