Coupling Variable Permeability to Strain and Mass Transfer in Contaminated Clays

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Summary

A constitutive law for variable permeability links it to an evolving microstructural flow pattern via mass conservation law for pore fluid. The flow pattern is based on actual porosimetry data and an idealized clay microstructure. Mass conservation takes into account chemo-elasto-plastic strain and mass removal from the solid phase induced by the permeation of clay with concentrated organic contaminant.

Introduction

Some inorganic and organic liquids at high concentration, such as ethanol, dioxane, carbon tetrachloride, xylene, acetic acid increase upon permeation into clay its permeability over up to four orders of magnitude in laboratory tests. These liquids are often highly toxic but commonly found in landfills, where they are usually poorly controlled. Their effect may become highly detrimental to the landfill liner permeability, even at a relatively low concentration, when they are associated with another liquid contaminant in which they are soluble, and which in turn, is soluble in water [1]. Numerical analyses show that, transport of contaminants in so exposed liner initially only diffusive and hence slow, may gradually develop advection, eventually dominating the whole transport, as permeability increases significantly as a result of diffusion.

On the other hand, Fernandez and Quigley [1] revealed that a simultaneous application of a relatively modest stress acting during contaminant flow across a liner may avert the negative effect of contaminants on permeability. They strongly advocate including the stress factor in the design considerations for the liners. A mechanical loading, in-place before the inflow of some organic chemicals, may induce chemical consolidation in clay sufficient to prevent any change in its hydraulic conductivity. Conversely, it is suggested that a decrease in effective confining stress occurring due to an increase in the level of leachate above the liner if leachate collection system fails may lead to permeability failure.

Our purpose is to examine links between permeability and change in pore structure due to simultaneous contamination and mechanically induced strain. We shall extend previous idealized microstructure model (Hueckel et al. [2]) in which no strains were taken into account. We postulate that there is a link between variable permeability and the variable volume of fluid phase of the material, which includes chemo-plastic strain.

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The volume of the fluid phase is then down-scaled to a particular microstructural flow pattern related to porosimetry data. Volume change of fluid phase is linked to contaminant specific, physico-chemical interaction between clay solids and fluid, in particular, interlamellar shrinking and flocculation.

Experimental Evidence

Some inorganic and organic liquids, especially ethanol, dioxane and acetic acid increase significantly clay permeability in laboratory tests. Ethanol produces more than two orders of magnitude increase while dioxane up to four. Increasing concentration of ethanol or dioxane produced a slight decrease in permeability, at 20-65% of volume concentration of the contaminant, followed by a relatively sharp increase at about 70-80% [1]. This occurs only under no load. Fernandez and Quigley [1] noticed also that a modest load applied during contaminant transport anihilates the effect of contaminants on permeability. This stress effect is concomitant with chemical consolidation. Pore size distribution data indicate that out of three pore modes, the largest (3 μm) nearly disappears, the intermediate (0.08 μm) somewhat increases in total volume, whereas the interlamellar pores decrease up to half of their size. Such evolution does not seem conducive to increase in permeability. This brings up the question of a link between change in permeability, strain or porosity changes, and other microstructural changes in soil, including changes induced by variable chemistry of pore fluid.

Theory

The central hypothesis in the proposed approach is that in saturated soils, permeability evolution, for a given type of microstructural evolution, is determined by the total volume of fluid phase, which in turn is subject to mass balance constraint. The microstructural model requires introduction of variables pertinent to that scale and suitably averaged to be set equal to macroscopic quantities. For a bi-phase material with several species in each phase subjected to contaminant induced mass transfers between the phases and chemo-elasto-plastic deformation such mass balance at the continuum level has been shown (Loret et al. [3]) to take form as follows

$$\delta \upsilon'_F = -\delta \varepsilon'^e_{vol} - \delta \varepsilon'^p_{vol} - \frac{1}{\rho_{wS}} \delta m'^{\,react}_{wS} \tag{1}$$

where primed variables represent macroscopic continuum quantities, as opposed to microscopic variables to be introduced further on. In particular υ'_F is defined as total volume of fluid phase per representative elementary volume (REV) of the entire medium

$$\delta \upsilon'_F = \frac{1}{\rho_{wF}} \left(\delta m'^{\,react}_{wF} + \delta m'^{\,trans}_{wF} \right) + \frac{1}{\rho_{cF}} \left(\delta m'^{\,react}_{cF} + \delta m'^{\,trans}_{cF} \right) \tag{2}$$

while each mass content m_{iJ}' is defined as

$$m'_{iJ} = \frac{M'_{iJ}}{V'_0}, \text{ no summation over } i \text{ and } J, \qquad (3)$$

where M'_{iJ} is mass of species i in the phase J within the REV. Species considered are: in solid phase, S: mineral, sS, adsorbed water, wS, and contaminant adsorbed to solid, cS; while in fluid phase, F: free water in pore fluid, wF, dissolved contaminant in pore fluid, cF and cations in pore fluid, caF. Lower index densities ρ_{iJ}, are intrinsic densities of the species. Superscripts *react* and *trans* refer to masse changes due to reactions or transport they undergo. Symbols ε_v^e and ε_v^p denote respectively the elastic and plastic component of the volumetric strain. They are known from the overall measurement of a continuum scale sample, whereas theoretically they are described by constitutive equations of associative chemoplasticity (Hueckel [4]).

We also assume that: (i) clay is a "extended strongly interacting mixture" [4]. Furthermore: species of the solid phase changing mass may do it only through reactions, this means that they cannot diffuse and thus that the contaminant moves only through free water. Most importantly, the adsorbed water cannot diffuse across the solid phase. The assumption of constant specific density of the species does not exclude the change of water density when it converts from adsorbed water into free water, or vice-versa.

Eq. (1) allows us to express the change of the volume of the fluid phase that determines the permeability change, in terms of strain, and adsorbed water mass exchange, which describes the non-deformational mass change of the solid phase. The first two terms of its rhs are known only on the macro-scale, through macroscopic plasticity, whereas the last term is known at the scale of platelets of clay. The lhs term will be used at the micro-scale to determine the size of fluid transporting vessels. The last term will be scaled up to the macro-scale via an averaging procedure:

$$m'_{wS} = (1-n)\langle\langle m_{wS}\rangle\rangle = (1-n)\frac{1}{V'}\int_{v_S} m_{wS}^{react}(m_{cF})dV_S; \quad \textit{no summation over indices} \quad (4)$$

where V_S is the volume of the solid phase, which, as defined before, contains variable amounts of the adsorbed water.

The loss mass of adsorbed water from the representative volume of soil may be dealt with by extrapolating from a nanoscale the behavior of a pair of platelets to that of an n-platelet cluster assuming that all platelets remain parallel and that the change in distance between the platelets is instantaneous and simultaneous. Using Poisson-Boltzman law for overlapping Diffuse Double Layers (DDL) characterized by: dielectric constant of free pore fluid, D_F, volume concentration, c_{caF}, of cations in pore water, and absolute temperature, T, one may predict the change of distance, t, between such platelets as

$$dt = \sqrt{\frac{kT}{2e^2v^2}} \sqrt{\frac{n_F}{D_F c_{caW}\left(1 - m_{cF}/\rho_{cF}\right)}} \left(\frac{\Delta D_{w,c}}{n_F \rho_F} - \frac{D_F}{n_{wF}\rho_{cF}}\right) dm_{cF} \qquad (5)$$

where k is Boltzman constant, e is elementary charge, and cation valence, v. For the moment, the pore solution is considered as homoionic. Cationic concentration as said before changes in proportion to concentration of water in pore fluid, or in other terms $c_{caW} = M_{caF}/V_w = const$. The dependence of D_F of pore fluid on its component concentrations is assumed to follow the rule of mixture, hence

$$D_F = D_w m_{wF} - D_c m_{cF}, \text{ and } \Delta D_{wc} = D_w - D_c. \qquad (6)$$

Experiments with replacement of water by ethanol show an initial increase of interlamellar spacing from 1.8 to 2.3 nm at concentration below 25% [5]. Then a two-step drop, first to 2.0 nm at 37% and then from 80 and 100% of ethanol to 1.6 nm occurs. The latter coincides with an increase in permeability at about 80% ethanol [1]. In dioxane, the collapse of interlamellar distance to the final 1.5 nm occurs at low concentrations. The incremental dependence of the interlamellar distance may be described

$$dt = E_D\left(D_F\right) dD_F \qquad (7)$$

where E_D is interlamellar expansivity coefficient defined piecewisely.

The upscaling to the macroscopic level of the variable of interlamellar fluid loss described by t, is accomplished using specific surface area. To evaluate the loss (gain) of interlamellar fluid, half of interlamellar surface area of platelets per unit weight of the dry solid, S_{sI}, will be considered only, as an interlayer is coated by two platelets. Hence,

$$dm'_{wS} = -\frac{1}{2} S_{sI} \rho_{sS} n_{sS} \rho_{wS} dt \qquad (8)$$

where dt can be obtained either from eq. (5) or (7).

The replacement of the pore water with organic fluid causes also flocculation of clay particles [5]. Ethanol caused flocculation occurs in the unconstrained conditions abruptly between 48 and 55% of concentration. Unconstrained conditions mean porosity allowing a free movement of particles. Dioxane produces a stronger flocculation. In compacted clay flocculation occurs as rotation of clusters. It may take place only if there is room available. Thus, rotation is postulated to be a function of the volume of void formed by cluster shrinkage and chemo-plastic strain per individual cluster. Such volume is assumed to be equal to the volume of fluid phase as calculated at the continuum (macroscopic) level from eq. (1). To convert it to microscopic quantity we postulate that

$$\upsilon'_F = n\langle\langle \upsilon_F \rangle\rangle = n\frac{1}{V'}\int_v \upsilon_F(\varepsilon_{vol}, m_{cF})dV \text{ ;no summation over the indices} \qquad (9)$$

and thus average microscopic change in fluid phase volume can be determined. Assuming a periodic clay structure, as in Fig. 1, an elementary fluid volume per individual cluster and its increment, Δv_F can be calculated from eq. (1, 8 and 9). Strain increments in eq. (1) are calculated following chemo-plasticity algorithms (see [4]).

A model for flow in unstressed clay as a system of slits with sizes corresponding to the two major actual pore modes found through porosimetry was proposed in [2]. The third, smallest pore mode, corresponding to interplatelet space is not considered, as filled with immobile water. The slit-type tubes are between clusters, arranged in series, Fig. 1. The larger pore mode (3 μm) is attributed to the (unstressed) channels between the clusters parallel to the major principal stress, while the smaller (about 15 times) one, to the stressed pores perpendicular to the major principal stress of compaction

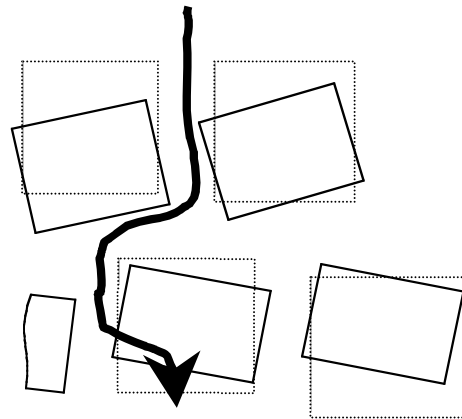Fig.1   Fig.2

Assuming that the entire change in pore fluid volume is equivalent on the microscale to the rotation of the walls of the horizontal (smaller) channels, Fig.2 the opening ratio of the two ends of the horizontal channel may be determined as

$$\frac{\left(\delta_2 - \delta_1^0\right)}{\delta_1^0} = 1 + \frac{\Delta v_F}{\mu N}\frac{1}{a^2\delta_1^0} \tag{10}$$

where δ_1^0 is a constant (smaller) entrance size of the cuniform channel, assumed as constant, N is the number of clusters in a REV, and μ is a configuration coefficient, which takes into account the proportion of clusters which are actually contributing to the formation of rotated channels. Thus, an enlarged entrance size can be obtained, and hence the permeability of the chemically affected clay under stress

$$K^f = \frac{(\delta^2)^3}{12h'} R \; ; where \quad R = 6\frac{h'}{\delta^2}\left[1-\left(\frac{\delta^2}{\delta^1}\right)^2\right]^{-1}\frac{1}{P*(\alpha)} \; and \; P* = \frac{3}{4\alpha} \cong \frac{3}{4}\frac{a'/\delta^1}{1-\left(\frac{\delta^2}{\delta^1}\right)} \quad (11)$$

where δ^1 and δ^2 are respectively entrance and exit openings of a horizontal channel, [3]. Further assumptions are made that rotation angles are small, namely $\alpha < 18º$. For the case of dioxane contamination tested in [1] at different level of stress, chemoplastic strain has been taken into account using eq.1-11, with their values as in [4]. The permeability variation at different concentrations at different stress levels is presented in Fig. 3.
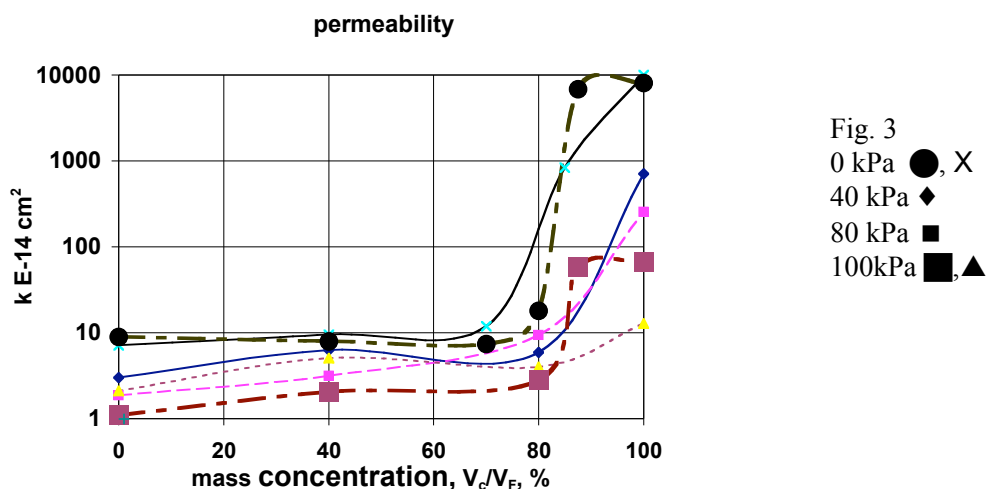
permeability

Fig. 3
0 kPa ●, X
40 kPa ◆
80 kPa ■
100kPa ■,▲

It is hence concluded that while the values at 100% are controlled by the chemoplastic strain, at the lower concentrations the controlling factor is flocculation.

References:

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