

Micro/Macro-Behavior of Water Flow and Diffusion in Clay: Multiscale Homogenization Analysis

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Abstract

Clay is a micro-inhomogeneous material. For bentonite clay we present here a unified numerical scheme to treat its molecular characteristics and micro/macro-continuum behavior. Note that we commonly use a macro-phenomenological model for analyzing material behavior. However, existing models are not sufficiently effective under extreme conditions such as deeply located clay. We try to resolve this difficulty.

Properties of saturated bentonite are characterized by hydrated montmorillonite, the major clay mineral of bentonite. Since the crystalline structure of clay minerals determines fundamental properties, we analyze its molecular behavior by applying a molecular dynamics (MD) simulation and inquire into physicochemical properties of the clay hydrate system such as diffusivity of chemical species. To extend the microscopic characteristics of constituent materials to the macroscopic diffusion behavior of the micro-inhomogeneous material we develop a multiscale homogenization analysis (HA) to treat adsorption behavior at a micro-level.

Key words: clay, diffusion, multi-component fluid, adsorption, seepage, molecular dynamics, multi-scale homogenization analysis

1. Introduction

Bentonite has an extremely low permeability. The existing model is not sufficiently effective for analyzing permeability and diffusion behavior, because it does not always reflect molecular-based true physical and chemical behavior, which essentially controls transport phenomena in bentonite. Classical analysis requires experimental-based parameters to be provided, but sometimes we cannot furnish such data. We note that the phenomenological model basically works for an interpolation-based prediction, and accurate experimental data is important for this model. A new scheme is required for analyzing the physical and chemical behavior of clay under extreme conditions, since the behavior is beyond the scope of the phenomenological concept of mechanics.

Bentonite clay is a micro-inhomogeneous material. It consists of clay minerals, macro-grains, water,

air, and others. Major properties of saturated bentonite clay are characterized by clay minerals and water.

Clay minerals of bentonite are mainly montmorillonite. One clay mineral is of a lamellar shape with the size of approximately $100 \times 100 \times 1$ nm, and several lamellae are gathered in a group together with interlamellar water. This hydrated clay mineral system gives a micro-scale structure in our analysis. Difficulties in clay-hydrate analysis lie in the poor crystallinity of a clay mineral.

Since the crystalline structure of a clay mineral determines the fundamental properties of the hydrate system, we analyze its molecular behavior by applying a molecular dynamics simulation method (MD; Kawamura & Ichikawa 2001), and we inquire into the physicochemical properties of the clay hydrate such as diffusivity of chemical species. Note

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that in our MD analysis we study a beidellite crystal, which belongs to the same smectitic mineral group as montmorillonite. The molecular formulation of the hydrated beidellite is given by $\text{Na}_{1/3}\text{Al}_2[\text{Si}_{11/3}\text{Al}_{1/3}]\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$.

The macro-grains consist mainly of quartz, and the average size is about $10\text{--}50\mu\text{m}$. This forms a meso-scale structure.

Since the size of a micro-scale structure (i.e., the clay hydrate) is very different from the size of the meso-scale structure (i.e., the macro-grains) and the macro-scale structure such as a clay stratum, we need to introduce a new theoretical scheme to combine the multi-scale structures. In this work we develop a multiscale homogenization analysis (HA) method for extending the microscopic characteristics of constituent materials to the macroscopic diffusion behavior of the micro-inhomogeneous material. Many papers on HA have been published for the behavior of porous media (Auriault & Lewandowska 1997, Hornung 1997), which are mostly based on the mixture theory of solid and water. Our method is not based on the mixture theory. We start with fundamental flow and diffusion equations, and derive meso-scale and macro-scale equations. The procedure developed gives sufficiently accurate results for the seepage and diffusion problem.

HA involves difficulty in specifying the micro-scale material properties. For this purpose we use MD results. Furthermore the adsorption property on the surface of clay minerals is essential for diffusion phenomena, and to treat such microscale behavior we need higher order terms of asymptotic expansion in HA. Note that before applying HA we summarize the existing diffusion models for soil. Then we present our model, which can treat micro-inhomogeneous properties with adsorption behavior on the surface of clay minerals.

2. Classical diffusion theory of multicomponent solution in saturated porous media

First we use classical diffusion theory of multiple chemical species (i.e., solutes) in a dilute solution and the diffusion in a porous media saturated with the solution, because it gives the fundamental reason why we need to introduce the micro/macro analysis

based on the molecular simulation and the homogenization method.

2.1 Diffusion of chemical species in solution

Let us think a dilute solution with n^* -components, in which $(1, 2, \dots, n^*-1)$ -components are solutes (i.e., diffusing chemical species), and the n^* -th component is solvent (i.e., water in our case). We introduce the following mass and molar fractions[†]

$$\text{mass fraction: } \phi_\alpha = \frac{m_\alpha}{m} \quad (1)$$

$$\text{mole fraction: } \chi_\alpha = \frac{n_\alpha}{n^*} \quad (2)$$

where m_α [g] and n_α [mol] are the mass and the amount of substance of the α -th component, respectively, with the total mass m and the total substance n^* :

$$\sum_{\alpha=1}^{n^*} m_\alpha = m, \quad \sum_{\alpha=1}^{n^*} n_\alpha = n^*. \quad (3)$$

Note that the sum of the above fractions is unity:

$$\sum_{\alpha=1}^{n^*} \phi_\alpha = 1, \quad \sum_{\alpha=1}^{n^*} \chi_\alpha = 1.$$

Let V be the total volume, and let M_α [g/mol] and M [g/mol] be the molar mass of the α -th component and the solution, respectively, given by

$$M_\alpha = \frac{m_\alpha}{n_\alpha}, \quad M = \frac{m}{n^*} \quad (4)$$

The mass density of the α -th component, ρ_α [kg/dm³], is given by

$$\rho_\alpha = \frac{m_\alpha}{V}, \quad (5)$$

and the average mass density of solution, ρ [kg/dm³], is

$$\rho = \sum_{\alpha=1}^{n^*} \rho_\alpha = \frac{\sum m_\alpha}{V} = \frac{m}{V}. \quad (6)$$

We now define the following concentrations (α : not summed):

$$\text{mass-percent concentration: } c_\alpha = \phi_\alpha = \frac{m_\alpha}{m} \quad (7)$$

$$\text{mass-volume concentration: } C_\alpha = \frac{m_\alpha}{V} = \rho_\alpha = \rho c_\alpha \quad (8)$$

$$\text{molar-mass concentration: } \bar{c}_\alpha = \frac{n_\alpha}{m_n} \quad (9)$$

$$\text{molar-volume concentration: } \bar{C}_\alpha = \frac{n_\alpha}{V} = \frac{\bar{C}_\alpha}{M_\alpha} \quad (10)$$

where m_n is the mass of solvent. The molar-volume concentration \bar{c}_α is usually called the molar concen-

[†] In classical mixture theory (Truesdell & Toupin 1960, Bowen 1976) the mass density ρ_α of the α -th constituent is defined as $m_\alpha(B) = \int_{\chi(B)} \rho_\alpha dv$ where $\chi(B)$ is the current configuration of the material body B . We here use an intuitive manner.

tration. If the solution is dilute ($m_n \approx m$), we have

$$\bar{c}_\alpha \approx \frac{n_\alpha}{m} = \frac{n_\alpha}{V} \frac{V}{m} = \frac{1}{\rho} \bar{C}_\alpha. \quad (11)$$

Note that the average mass-volume concentration C is related to the average molar-volume concentration \bar{C} and the average mass density ρ by

$$\rho = C = M\bar{C}; \quad C = \sum_{\alpha=1}^n C_\alpha, \quad \bar{C} = \sum_{\alpha=1}^n \bar{C}_\alpha \quad (12)$$

For the dilute solution given by Eqn(11) we have

$$\bar{c} \approx \frac{1}{M}, \quad \bar{c} = \sum_{\alpha=1}^n \bar{c}_\alpha.$$

Now applying Reynolds' transport theorem yields

$$\begin{aligned} \frac{d^\alpha}{dt} \int_\Omega \rho_\alpha dv + \int_\Omega \dot{\gamma}_\alpha dv \\ = \int_\Omega \left[\frac{\partial \rho_\alpha}{\partial t} + \frac{\partial}{\partial x_i} (\rho_\alpha v_i^\alpha) + \dot{\gamma}_\alpha \right] dv = 0 \end{aligned} \quad (13)$$

where v_i^α is the velocity of the α -th component particles, $d^\alpha \phi / dt = \partial \phi / \partial t + \partial(\phi v_i^\alpha) / \partial x_i \equiv \dot{\phi}$ implies the material time derivative of a function ϕ with respect to the α -th component, and $\dot{\gamma}_\alpha$ gives the source term per volume per unit time because of chemical reactions, *etc.* Referring to Eqn(8) the local form in terms of the mass-percent concentration is then written as

$$\begin{aligned} \frac{\partial \rho_\alpha}{\partial t} + \frac{\partial}{\partial x_i} (\rho_\alpha v_i^\alpha) + \dot{\gamma}_\alpha \\ = \frac{\partial(\rho c_\alpha)}{\partial t} + \frac{\partial}{\partial x_i} (\rho c_\alpha v_i^\alpha) + \dot{\gamma}_\alpha = 0. \end{aligned} \quad (14)$$

Summing up all components with respect to α yields

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i} (\rho v_i) = 0 \quad (15)$$

where the average velocity v is defined by

$$v \equiv \frac{1}{\rho} \sum_{\alpha=1}^n \rho_\alpha v^\alpha = \frac{1}{\rho} \sum_{\alpha=1}^n C_\alpha v^\alpha = \sum_{\alpha=1}^n c_\alpha v^\alpha, \quad (16)$$

and the average source term $\dot{\gamma}$ vanishes because of the mass conservation law:

$$\dot{\gamma} = \sum_{\alpha=1}^n \dot{\gamma}_\alpha = 0.$$

Let us introduce a diffusing mass flux j^α of the α -th component by

$$j^\alpha \equiv \rho_\alpha (v^\alpha - v) = C_\alpha (v^\alpha - v) = \rho c_\alpha (v^\alpha - v). \quad (17)$$

Then the mass conservation equation (14) together with incompressibility of the whole solution, $\partial v_i / \partial x_i = 0$, gives

$$\frac{\partial(\rho c_\alpha)}{\partial t} + v_i \frac{\partial(\rho c_\alpha)}{\partial x_i} + \frac{\partial j_i^\alpha}{\partial x_i} + \dot{\gamma}_\alpha = 0. \quad (18)$$

The mass flux j^α is given as the sum of molecular diffusion, pressure diffusion, and thermal diffusion, in which molecular diffusion is important for the dilute solution. Then we have the following Fick's

first law of diffusion:

$$j_i^\alpha = -\rho \sum_{\beta=1}^n D_{ij}^{\alpha\beta} \frac{\partial C_\beta}{\partial x_j}. \quad (19)$$

Substituting this into Eqn(18) yields

$$\frac{\partial c_\alpha}{\partial t} + v_i \frac{\partial c_\alpha}{\partial x_i} - \frac{\partial}{\partial x_i} \left(\sum_{\beta=1}^n D_{ij}^{\alpha\beta} \frac{\partial c_\beta}{\partial x_j} \right) + \dot{\gamma}_\alpha^* = 0 \quad (20)$$

where we set $\dot{\gamma}_\alpha^* = \dot{\gamma}_\alpha / \rho$.

2.2 Diffusion problem of multicomponent solution in saturated porous media

Here we use classical diffusion theory for a multicomponent dilute solution in a saturated porous media with porosity n .

Let Γ_{fs} be a fluid-solid interface in micro-level, and ζ_i^α the mass flux of the α -th component on Γ_{fs} adsorbed from solution. Referring to Eqns (13) and (14), we have the following mass conservation equation for the α -th component of solution:

$$\begin{aligned} \frac{d^\alpha}{dt} \int_\Omega n \rho_\alpha dv + \int_\Omega n \dot{\gamma}_\alpha dv - \int_{\Gamma_{fs}} \zeta_i^\alpha n_i ds \\ = \int_\Omega \left[\frac{\partial(n \rho c_\alpha)}{\partial t} + \frac{\partial}{\partial x_i} (n \rho c_\alpha v_i^\alpha) + n \dot{\gamma}_\alpha \right] dv \\ - \int_{\Gamma_{fs}} \zeta_i^\alpha n_i ds = 0 \end{aligned} \quad (21)$$

where ρ is the average mass density given by Eqn(6), c_α the mass-percent concentration of the α -th component, v^α the particle velocity, $\dot{\gamma}_\alpha$ the source term due to chemical reaction, *etc.* and n_i the unit outward normal on Γ_{fs} . Let us define the average velocity v by Eqn(16), then the mass flux j^α of the α -th component can be written as

$$j^\alpha \equiv n \rho_\alpha [v^\alpha - (v - v^s)] = n \rho c_\alpha [v^\alpha - (v - v^s)]$$

where v^s is the particle velocity of a solid phase. Usually, the solid velocity v^s is very small ($|v^s| \ll 1$), so we can write

$$j^\alpha \approx n \rho c_\alpha (v^\alpha - v). \quad (22)$$

We now think of a mechanical dispersion of the α -th component in porous media caused by a forced local flow (Fig. 1). Let \bar{v} and \bar{c}_α be average velocity and concentration, respectively, and let \dot{v} and \dot{c}_α be deviations of velocity and concentration, respectively. Setting $c_\alpha = \bar{c}_\alpha + \dot{c}_\alpha$ and $v = \bar{v} + \dot{v}$ yield

$$\bar{c}_\alpha \bar{v} = \bar{c}_\alpha \bar{v} + \bar{c}_\alpha \dot{v}$$

because $\bar{c}_\alpha \dot{v} = \bar{v} \dot{c}_\alpha = 0$. Then we can introduce dispersive flux $j^{m\alpha}$ as

$$j^{m\alpha} = \bar{c}_\alpha \dot{v}. \quad (23)$$

Average velocity \bar{v} and average concentration \bar{c}_α can now formally be written as v and c_α , respectively. And, with Eqns(22) and (23) we have

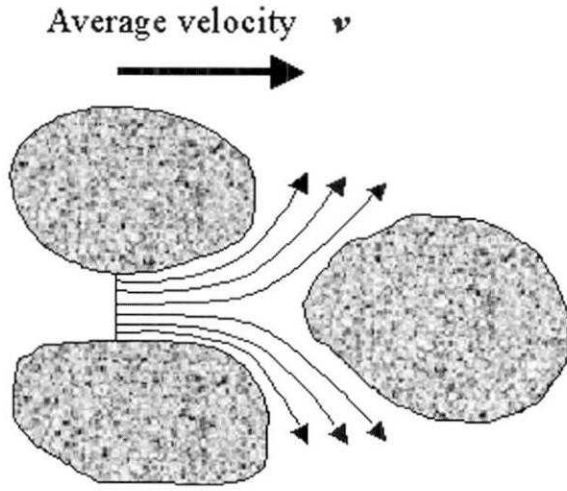


Fig. 1. Mechanical dispersion.

$$n\rho c_\alpha v^\alpha = j^\alpha + j^{m\alpha} + n\rho c_\alpha v. \quad (24)$$

Assuming the incompressibility of the solution $\partial v_i / \partial x_i = 0$, the mass conservation law (21) gives

$$\int_\Omega \left[\frac{\partial(n\rho c_\alpha)}{\partial t} + v_i \frac{\partial}{\partial x_i} (n\rho c_\alpha) + \frac{\partial \tilde{j}_i^\alpha}{\partial x_i} + n\dot{\gamma}_\alpha \right] dv - \int_{\Gamma_{fs}} \zeta_i^\alpha n_i ds = 0 \quad (25)$$

where we set $\tilde{j}^\alpha = j^\alpha + j^{m\alpha}$.

In our case we define that the 1st to $(n^* - 1)$ -th components are solutes, and the n^* -th component is water (that is, a solvent). We treat the case that the α -th constituent species (i.e., a solute) migrates into the solid-phase. However, we do not consider a diffusion phenomenon in the solid directly. We treat it in relation to the time-change of the solid-phase concentration. Then we are able to represent adsorption using the concentration of a *distribution factor* (see below for further details). We assume the following:

- 1) The amount of migration of the α -th component is small, so the mass density ρ_s of the solid is not changed significantly.
- 2) The velocity v^s of the solid can be ignored in practice ($|v^s| \ll 1$).
- 3) Molar diffusion of the α -th component in the solid may not be considered.

Then the conservation law of the α -th component in the solid can be written as

$$\int_\Omega \left[\frac{\partial(1-n)\rho_s c_\alpha^*}{\partial t} + (1-n)\dot{\gamma}_\alpha^* \right] dv + \int_{\Gamma_{fs}} \zeta_i^\alpha n_i ds = 0 \quad (26)$$

where c_α^* is the mass-percent concentration of the α -th component in the solid, and $\dot{\gamma}_\alpha^*$ is the source term of the α -th component in the solid.

Summing up Eqn (25) and (26) yields

$$\frac{\partial(n\rho c_\alpha)}{\partial t} + v_i \frac{\partial}{\partial x_i} (n\rho c_\alpha) + \frac{\partial \tilde{j}_i^\alpha}{\partial x_i} + n\dot{\gamma}_\alpha + \frac{\partial(1-n)\rho_s c_\alpha^*}{\partial t} + (1-n)\dot{\gamma}_\alpha^* = 0, \quad (27)$$

because the surface integral terms are canceled out.

Let n be *effective porosity*, which is directly related to diffusion. If we treat only the isotropic diffusion case ($D_{ij}^{\alpha\beta} = D_{\alpha\beta} \delta_{ij}$), the mass flux of the α -th component can be represented by Fick's first law:

$$j_i^\alpha = -\rho n \sum_{\beta=1}^{n^*} D_{\alpha\beta}^e \frac{\partial c_\beta}{\partial x_j} \quad (28)$$

where $D_{\alpha\beta}^e$ is the effective diffusion coefficient, which is related to the molecular diffusion coefficient $D_{\alpha\beta}$ by

$$D_{\alpha\beta}^e = \frac{\delta}{\tau} D_{\alpha\beta}. \quad (29)$$

Here $\tau (>1)$ is called as *tortuosity*, which may be given with relation to the shortest path l and the effective path l_e by

$$\tau = \left(\frac{l_e}{l} \right)^2 > 1. \quad (30)$$

$\delta (\leq 1)$ is the *constrictivity* of pores with the average radius d_p , and the effect must be considered in the case that there are truly fine pores, which are compatible with the radius d_m of solute molecules. That is, if we have

$$\lambda_p = \frac{d_m}{d_p} < 1, \quad (31)$$

the following experimental equations have been proposed:

$$\delta = (1 - \lambda_p)^2 (1 - 2.104 \lambda_p + 2.09 \lambda_p^3 - 0.95 \lambda_p^5) \quad (\text{Renkin 1954})$$

$$\delta = (1 - \lambda_p)^4 \quad (\text{Beck and Schlitz 1970})$$

$$\delta = \exp(-4.6 \lambda_p) \quad (\text{Satterfield and Colton 1973})$$

$$\delta = 1.03 \exp(-4.5 \lambda_p) \quad (\text{Chantong and Massoth 1983})$$

In Eqns(28) and (29) the coefficient

$$F = n \frac{\delta}{\tau}$$

is sometimes called as the *formation factor*, which is related to the *representative elementary volume* (REV). Let D_0^α be the diffusivity of the α -component in pure water, then we may define

$$D_{\alpha\beta} = \alpha^* D_0^\alpha \delta_{\alpha\beta} \quad (\alpha: \text{not summed})$$

where α^* gives the solute coefficient. Then Fick's law (28) can be written as

$$\tilde{j}_i^\alpha = -\rho D^e(c^\alpha) \frac{\partial c_\alpha}{\partial x_i} = -\rho n D^{e*}(c^\alpha) \frac{\partial c_\alpha}{\partial x_i} \quad (32)$$

$$\begin{aligned} D^e(c^\alpha) &= n D^{e*}(c^\alpha) = \alpha^* F D_\delta^\dagger \\ &= \alpha^* n \frac{\delta}{\tau} D_\delta^\dagger \quad (\alpha: \text{not summed}). \end{aligned} \quad (33)$$

We introduce a working hypothesis that the flux caused by a mechanical dispersion, $\tilde{j}^{m\alpha}$, can be written in the same form as Fick's first law:

$$\tilde{j}_i^{m\alpha} = -\rho D_{ij}^{m\alpha}(c^\alpha) \frac{\partial c_\alpha}{\partial x_j} = -\rho n D_{ij}^{m\alpha*}(c^\alpha) \frac{\partial c_\alpha}{\partial x_j} \quad (34)$$

$$D_{ij}^{m\alpha}(c^\alpha) = n D_{ij}^{m\alpha*}(c^\alpha) \quad (35)$$

where we consider the anisotropic characteristics. From experiments the coefficients $D_{ij}^{m\alpha}(c^\alpha)$ are given by

$$D_{ij}^{m\alpha}(c^\alpha) = \left\{ a_T v \delta_{ij} + (a_L - a_T) \frac{v_i v_j}{v} \right\} f(\text{Pe}, \delta, c^\alpha) \quad (36)$$

where a_T and a_L are transversal and longitudinal dispersivities, respectively, $v = |\mathbf{v}|$, Pe Peclet number, and δ constrictivity. The function $f(\text{Pe}, \delta, c^\alpha)$ may be given as

$$f(\text{Pe}, \delta, c^\alpha) = \frac{\text{Pe}}{(\text{Pe} + 2 + 4\delta^2)},$$

but usually we can assume that (Bear & Verruijt 1987)

$$f(\text{Pe}, \delta, c^\alpha) \simeq 1.$$

Mass flux $\tilde{\mathbf{j}}^\alpha$ coupled with molecular diffusion and mechanical dispersion can finally be written as

$$\tilde{\mathbf{j}}^\alpha \equiv \tilde{\mathbf{j}}^\alpha + \tilde{\mathbf{j}}^{m\alpha} = -\rho \tilde{D}_{ij}^e(c^\alpha) \frac{\partial c_\alpha}{\partial x_j} = -\rho n \tilde{D}_{ij}^{e*}(c^\alpha) \frac{\partial c_\alpha}{\partial x_j} \quad (37)$$

$$\tilde{D}_{ij}^e(c^\alpha) = D^e \delta_{ij}(c^\alpha) + D_{ij}^{m\alpha}(c^\alpha) = n \tilde{D}_{ij}^{e*}(c^\alpha),$$

$$\tilde{D}_{ij}^{e*}(c^\alpha) = D^{e*}(c^\alpha) \delta_{ij} + D_{ij}^{m\alpha*}(c^\alpha). \quad (38)$$

Now let us consider adsorption in a porous media, which is classified into *physisorption* due to the Coulomb and van der Waals forces and the chemisorption followed by a surface reaction. The heat of the physisorption ranges from 300 to 3,000 J/mol, while the heat of the chemisorption is from 40 to 400 KJ/mol. The rate of adsorption varies greatly under the conditions of the hydrogen ion exponent pH and the redox potential Eh.

An *adsorption isotherm* describes the chemical reaction procedure of solutions at a constant temperature. The thermodynamics theory only gives an equilibrium procedure (i.e., an *equilibrium adsorption isotherm*), and a *nonequilibrium adsorption isotherm* may be described in a phenomenological form in which an activity energy due to the reaction is generally ignored, and the rate of adsorption may be given

as a function of fluid velocity.

Let the current volume of an adsorbed layer be V , and let the final volume of the layer after completion of the reaction be V_∞ . Then the fractional coverage θ is expressed as

$$\theta = \frac{V}{V_\infty}. \quad (39)$$

We here treat a typical classical example, called the Langmuir isotherm (Langmuir 1918, Atkins 1998). We introduce the following assumptions:

- 1) Adsorption proceeds with monolayer coverage.
- 2) On the perfectly flat surface there are a total of N -sites of adsorption, which are uniformly distributed on the surface, and are mutually equivalent.
- 3) A molecule adsorbed on a site does not affect neighboring sites.

The rate of change of surface coverage is assumed to be proportional to the partial pressure p_α of the α -th component and the number of vacant sites $N(1-\theta)$:

$$\frac{d\theta}{dt} = k_a p_\alpha N(1-\theta)$$

On the other hand, the rate of change of adsorption may be proportional to the sites covered:

$$\frac{d\theta}{dt} = k_d N \theta.$$

At equilibrium both must be same:

$$k_a p_\alpha N(1-\theta) = k_d N \theta,$$

so we have

$$\theta = \frac{k_a p_\alpha}{k_d + k_a p_\alpha} = \frac{b p_\alpha}{1 + b p_\alpha} \quad (40)$$

where $b = k_a/k_d$ is called the adsorption factor:

In Eqn(40) for the case $b p_\alpha \ll 1$ (that is, if the partial pressure or the rate of adsorption is very small), we have

$$\theta = b p_\alpha. \quad (41)$$

This gives the well known *linear adsorption isotherm*.

For a dilute solution the mass-percent concentration c_α is proportional to the partial pressure p_α , so for the flow of a dilute fluid in a porous media from Eqn (40) we have

$$c_\alpha^* = \frac{b c_\alpha}{1 + b c_\alpha} \quad (42)$$

where c_α^* is the concentration of the α -th component in the solid given in Eqn(27), and c_α the concentration in the fluid. Then the linear adsorption isotherm (41) can be written as

$$c_a^* = K_d c_a \quad (43)$$

where $K_d (=b)$ is called the *distribution coefficient* or *partitioning coefficient*.

Let us assume that the solid matrix and the fluid are incompressible ($\rho = \text{constant}$, $\rho_s = \text{constant}$) and that the solid skeleton is not deformable ($n = \text{constant}$). Substituting Fick's law (37) and the linear adsorption isotherm equation (43) into the diffusion equation (27) yields

$$nR_d \frac{\partial c_a}{\partial t} + \bar{v}_i \frac{\partial c_a}{\partial x_i} - \frac{\partial}{\partial x_i} \left(\tilde{D}_{ij}^*(c^a) \frac{\partial c_a}{\partial x_j} \right) + \dot{\gamma}_a^* = 0 \quad (44)$$

where \bar{v} is the seepage velocity defined by

$$\bar{v}_i = n v_i$$

and

$$R_d = 1 + \frac{(1-n)\rho_s K_d}{n\rho} \quad (>1) \quad (45)$$

is called the retardation factor. Eqn(44) is equivalent to

$$R_d \frac{\partial c_a}{\partial t} + v_i \frac{\partial c_a}{\partial x_i} - \frac{\partial}{\partial x_i} \left(\tilde{D}_{ij}^*(c^a) \frac{\partial c_a}{\partial x_j} \right) + \dot{\gamma}_a^* = 0. \quad (46)$$

Note that the source term $\dot{\gamma}_a^*$ or $\dot{\gamma}_a^*$ is given by

$$\dot{\gamma}_a^* = n \dot{\gamma}_a^* = \frac{n}{\rho} \left[\dot{\gamma}_a + \frac{1-n}{n} \dot{\gamma}_a^s \right].$$

3. Molecular dynamics simulations of clay hydrate for pure- and salt-water

Physical properties of clay minerals are difficult to understand by means of experimental methods, because of their fine structure and poor crystallinity. We have applied molecular simulation methods for

specifying physical and chemical properties of clay hydrate. The key issue for the molecular simulation is how to determine the interatomic or intermolecular interactions quantitatively. Here we use a new empirical interatomic potential model (Kawamura *et al.* 1997, Ichikawa *et al.* 1999). Since the details of MD simulation applied for clay hydrate are found in Kawamura & Ichikawa 2001, we do not repeat them.

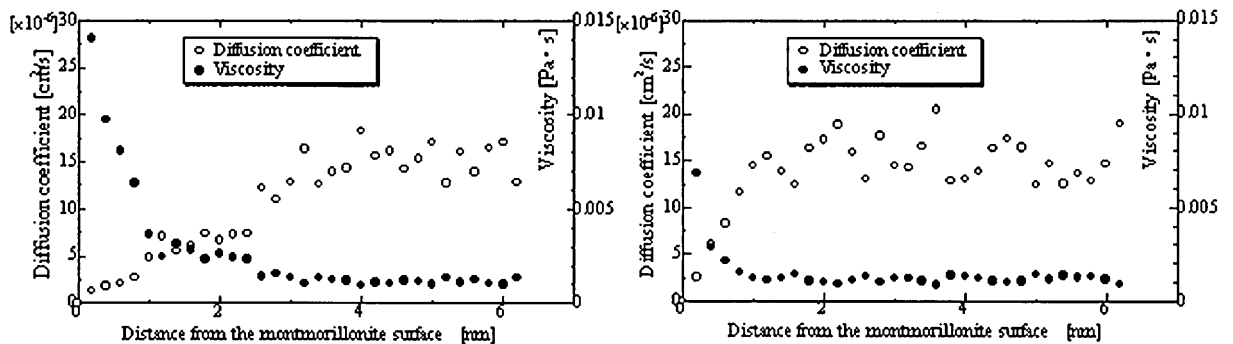
We can calculate a wide variety of physical properties such as elastic moduli, viscosity, heat capacity, and heat conductivity by applying the standard statistical thermodynamics procedure for the MD results. For example, shearing viscosity along layers is calculated in Table 1.

For calculating diffusivity and viscosity of pure- and salt-water in the neighborhood of a clay mineral we use MD models which include one clay-mineral layer and surrounding water molecules. The latter case is equivalent to the composition of seawater. An (NVE)-ensemble MD (V the volume and E the internal energy) is carried out. To calculate the diffusivity of water near the clay mineral surface we divide the water part into slices with ca. 0.2 nm thickness. Using MD results we first calculate the mean square displacement (m.s.d.) for each slice, then the diffusivity (i.e., the slope of m.s.d.) is obtained. Next, by applying the Stokes-Einstein relationship with its diffusing spare $\delta = 0.152$ [nm], which is obtained by our MD model for pure water (without clay mineral), the viscosity of water at each sliced region is determined. Figure 2(a) shows diffusion coefficient and viscosity for pure water in each slice, and Fig. 2(b) shows them for saltwater.

We find the structurally ordered water layer in contact with the clay-surface, which is called the 'ice

Table 1. Calculated shearing viscosity of 1H₂O clay hydrate.

Shear rate	[1/ps]	0.1	0.01	0.001	0.0001
Viscosity	$\times 10^{-3}$ [Pa s]	0.42	1.40	2.40	8.00



(a) Diffusivity and viscosity of the external pure water. (b) Diffusivity and viscosity of the external saltwater.

Fig. 2. Distribution of diffusivity and viscosity in pure- and salt-water.

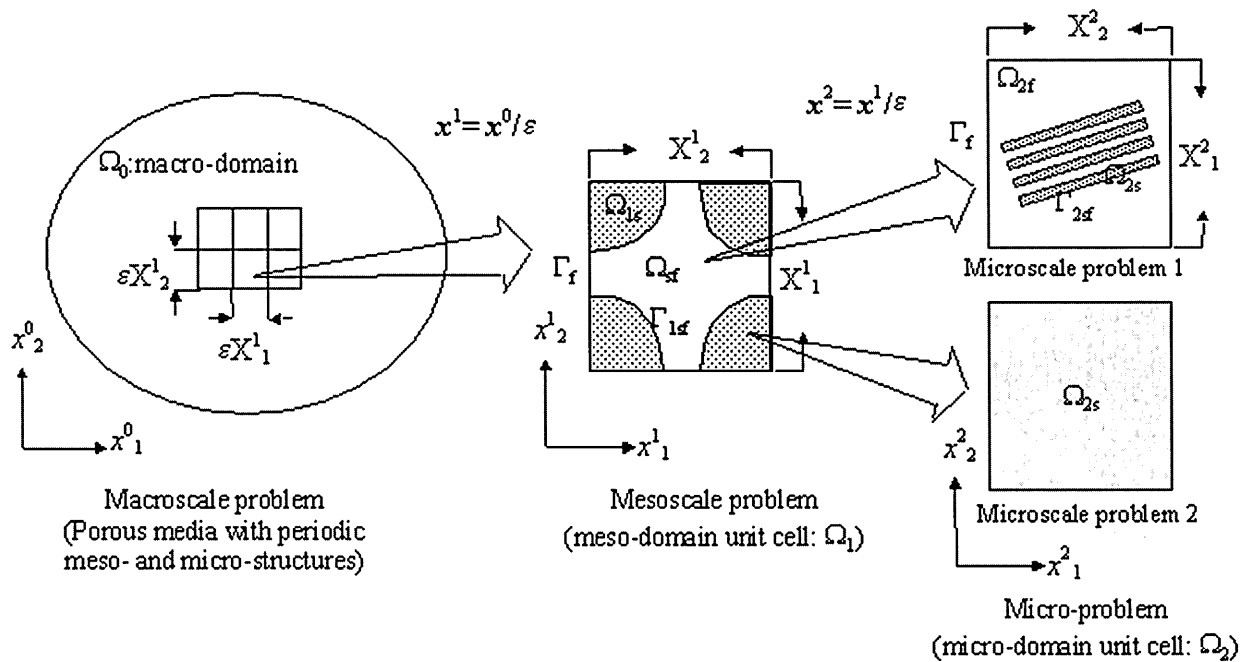


Fig. 3. Multiscale homogenization problem.

sheet'. The thickness of the ice sheet is ca. 0.5 nm for the pure water case, and is equivalent to approximately two layers of water molecules. In the 3–4 nm thick layer, the diffusion coefficient is changed rapidly. The viscosity is also changed in this layer. We call such a water property the *iceberg effect*. In the saltwater case the ice sheet becomes thinner with a weaker iceberg effect, as shown in Fig. 2(b).

4. Multiscale homogenization analysis of flow problem in porous media with distributed water viscosity

For the diffusion problem we need to know the local and global flow profiles in the porous media. For this purpose we develop a multiscale homogenization analysis (HA), which is a perturbation theory developed to study a micro-inhomogeneous material with periodic mesoscale and microscale structures. We apply the multiscale HA to the seepage problem in bentonite for pure- and salt-water with distributed water viscosity in the vicinity of clay minerals. Starting with Stokes' equation, one can obtain Darcy's law and a macroscopic seepage equation including the effects of the spatial distribution of viscosity.

4.1 Multiscale HA formulation of seepage problem with distributed viscosity

We consider a flow problem in porous media whose mesoscale and microscale domains are periodic (Fig. 3). Here the fluid phase is given as Ω_f , the solid phase as Ω_s , the fluid-solid mixed phase (the domain filled with lamellae of clay hydrate in the mesoscale problem) as Ω_{sf} , the interface of fluid and solid as Γ_{sf} , and the periodic boundary of the fluid phase as Γ_f .

Let \mathbf{x}^0 , \mathbf{x}^1 , and \mathbf{x}^2 be the macro-, meso-, and micro-scale coordinate systems, respectively. If we perform a laboratory seepage and consolidation test on typical Japanese bentonite, Kunigel V1, the macroscale specimen is 10^{-1} m, the mesoscale quartz grains are 10^{-4} m, and the microscale clay minerals are 10^{-8} m. So, we estimate $\varepsilon = 10^{-4}$, and introduce the following relations for the coordinate systems:

$$\mathbf{x}^1 = \frac{\mathbf{x}^0}{\varepsilon}, \quad \mathbf{x}^2 = \frac{\mathbf{x}^1}{\varepsilon}. \quad (47)$$

A cell in the mesoscale is of the size $|\mathbf{X}^1| = \varepsilon |\mathbf{X}^2|$, and a cell in the microscale is of the size $|\mathbf{X}^2|$.

Since the flow velocity is very slow in bentonite, the flow field is given by the following incompressible Stokes equation:

$$-\frac{\partial P^e}{\partial x_i} + \frac{\partial}{\partial x_j} \left(\eta \frac{\partial V_i^e}{\partial x_j} \right) + F_i = 0 \quad (48)$$

$$\frac{\partial V_i^e}{\partial x_i} = 0 \quad (49)$$

where V_i^e is velocity vector with shearing viscosity η which varies from place to place, P^e pressure, F_i body force vector, and Ω_{ef} water flow region in the global coordinate system (Γ_{ef} its boundary). The superscript^e implies field variables that rapidly fluctuate because of the micro-inhomogeneity. Note $V^e=0$ on the fluid-solid interface.

Since we have multiscale coordinate systems \mathbf{x}^0 , \mathbf{x}^1 , \mathbf{x}^2 , the original \mathbf{x} in Eqn (48) and (49) can be written as

$$\mathbf{x}=\mathbf{x}(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2), \quad (50)$$

and the partial differentiation changes to

$$\frac{\partial}{\partial x_i}=\frac{\partial}{\partial x_i^0}+\frac{1}{\varepsilon} \frac{\partial}{\partial x_i^1}+\frac{1}{\varepsilon^2} \frac{\partial}{\partial x_i^2} \quad (51)$$

We introduce an asymptotic expansion

$$\begin{aligned} V^e(\mathbf{x}) &= \varepsilon^4 V^0(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2) + \varepsilon^5 V^1(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2) \\ &+ \varepsilon^6 V^2(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2) + \dots, \end{aligned} \quad (52)$$

$$\begin{aligned} P^e(\mathbf{x}) &= P^0(\mathbf{x}^0) + \varepsilon P^1(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2) \\ &+ \varepsilon^2 P^2(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2) + \dots, \end{aligned} \quad (53)$$

where $V^\alpha(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2)$ and $P^\alpha(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2)$ ($\alpha=0, 1, \dots$) are X^1 -/ X^2 -periodic functions such as

$$\begin{aligned} V^\alpha(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2) &= V^\alpha(\mathbf{x}^0, \mathbf{x}^1 + \mathbf{X}^1, \mathbf{x}^2), \\ V^\alpha(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2) &= V^\alpha(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2 + \mathbf{X}^2) \\ P^\alpha(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2) &= P^\alpha(\mathbf{x}^0, \mathbf{x}^1 + \mathbf{X}^1, \mathbf{x}^2), \\ P^\alpha(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2) &= P^\alpha(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2 + \mathbf{X}^2) \end{aligned}$$

Note that for the asymptotic expansion given by Eqn (52) we start with the term ε^4 , since we intend to have a normalized Stokes' equation in microscale, which is shown later. Furthermore, it is assumed that P^0 is a function of only the macroscale coordinates \mathbf{x}^0 .

Substituting Eqn(51), (52) and (53) into Eqn (48) yields

$$\begin{aligned} &-\frac{\partial P^e}{\partial x_i} + \frac{\partial}{\partial x_j} \left(\eta \frac{\partial V_i^e}{\partial x_j} \right) + F_i \\ &= -\varepsilon^{-2} \frac{\partial P^0}{\partial x_i^2} - \varepsilon^{-1} \left(\frac{\partial P^0}{\partial x_i^1} + \frac{\partial P^1}{\partial x_i^2} \right) \\ &- \left(\frac{\partial P^0}{\partial x_i^0} + \frac{\partial P^1}{\partial x_i^1} + \frac{\partial P^2}{\partial x_i^2} \right) + \dots \\ &+ \frac{\partial}{\partial x_j^2} \left(\eta \frac{\partial V_i^0}{\partial x_j^2} \right) + \varepsilon \left[\frac{\partial}{\partial x_j^1} \left(\eta \frac{\partial V_i^0}{\partial x_j^1} \right) \right. \\ &\left. + \frac{\partial}{\partial x_j^2} \left\{ \eta \left(\frac{\partial V_i^0}{\partial x_j^1} + \frac{\partial V_i^1}{\partial x_j^2} \right) \right\} \right] + \dots + F_i \\ &= 0, \end{aligned}$$

and taking $\varepsilon \rightarrow 0$ yields

$$\varepsilon^{-2}\text{-term: } \frac{\partial P^0}{\partial x_i^2} = 0 \quad (54)$$

$$\varepsilon^{-1}\text{-term: } \frac{\partial P^0}{\partial x_i^1} + \frac{\partial P^1}{\partial x_i^2} = 0 \quad (55)$$

$$\varepsilon^0\text{-term: } \frac{\partial}{\partial x_j^2} \left(\eta \frac{\partial V_i^0}{\partial x_j^2} \right) - \frac{\partial P^2}{\partial x_i^2} = \frac{\partial P^0}{\partial x_i^0} + \frac{\partial P^1}{\partial x_i^1} - F_i \quad (56)$$

Since P^0 is a function only of \mathbf{x}^0 , Eqn (54) is automatically satisfied. Substituting this result into Eqn(55) yields

$$P^1 = P^1(\mathbf{x}^0, \mathbf{x}^1) \quad (57)$$

The right-hand-side term of Eqn (56) is independent of the microscale coordinate system \mathbf{x}^2 , because F_i is a function of \mathbf{x}^0 . Thus we can introduce normalized characteristic functions $v_i^k(\mathbf{x}^2)$, $p^k(\mathbf{x}^2)$ by

$$V_i^0 = - \left(\frac{\partial P^0}{\partial x_k^0} + \frac{\partial P^1}{\partial x_k^1} - F_k \right) v_i^k(\mathbf{x}^2) \quad (58)$$

$$P^2 = - \left(\frac{\partial P^0}{\partial x_k^0} + \frac{\partial P^1}{\partial x_k^1} - F_k \right) p^k(\mathbf{x}^2). \quad (59)$$

Here $v_i^k(\mathbf{x}^2)$ and $p^k(\mathbf{x}^2)$ are the *velocity characteristic function* and the *pressure characteristic function*, respectively. Substituting these into Eqn (56) yields the following *microscale Stokes' equation*:

$$\frac{\partial}{\partial x_j^2} \left(\eta \frac{\partial v_i^k}{\partial x_j^2} \right) - \frac{\partial p^k}{\partial x_i^2} + \delta_{ki} = 0 \quad \text{in } \Omega_2 \quad (60)$$

where δ_{ki} is the Kronecker's δ .

The incompressible condition (49) under the transformation laws (50) and (51) gives

$$\begin{aligned} \frac{\partial V_i^e}{\partial x_i} &= \varepsilon^2 \frac{\partial V_i^0}{\partial x_i^2} + \varepsilon^3 \left(\frac{\partial V_i^0}{\partial x_i^1} + \frac{\partial V_i^1}{\partial x_i^2} \right) \\ &+ \varepsilon^4 \left(\frac{\partial V_i^0}{\partial x_i^0} + \frac{\partial V_i^1}{\partial x_i^1} + \frac{\partial V_i^2}{\partial x_i^2} \right) + \dots = 0. \end{aligned}$$

As $\varepsilon \rightarrow 0$ this implies

$$\varepsilon^2\text{-term: } \frac{\partial V_i^0}{\partial x_i^2} = 0 \quad (61)$$

$$\varepsilon^3\text{-term: } \frac{\partial V_i^0}{\partial x_i^1} + \frac{\partial V_i^1}{\partial x_i^2} = 0 \quad (62)$$

$$\varepsilon^4\text{-term: } \frac{\partial V_i^0}{\partial x_i^0} + \frac{\partial V_i^1}{\partial x_i^1} + \frac{\partial V_i^2}{\partial x_i^2} = 0 \quad (63)$$

Substituting the characteristic function (58) into Eqn (61) yields the following *microscale incompressible equation*:

$$\frac{\partial v_i^k}{\partial x_i^2} = 0 \quad \text{in } \Omega_2. \quad (64)$$

Under the X^2 -periodic condition we solve the microscale equations (60) and (64) to determine the characteristic functions $v_i^k(\mathbf{x}^2)$ and $p^k(\mathbf{x}^2)$.

Next, we introduce a volume average in the microscale domain $\langle \cdot \rangle_2$ for v_i^k to get the *mesoscale homogenized permeability* K_{ji}^2 :

$$K_{ji}^2 = \left\langle v_i^j \right\rangle_2 = \frac{1}{|\Omega_2|} \int_{\Omega_2} v_i^j d\mathbf{x}^2. \quad (65)$$

Let us consider a weak form of the microscale Stokes' equation (60):

$$\left\langle -\eta \frac{\partial v_i^k}{\partial x_j^2} + p_i^k \delta_{ij}, \frac{\partial w_i}{\partial x_j^2} \right\rangle + \left\langle \delta_{ki}, w_i \right\rangle = 0, \quad \forall \mathbf{w} \in \mathbf{V}_{x^2} \quad (66)$$

where

$\mathbf{V}_{x^2} = \{\mathbf{u} \in (H^1(\Omega_{2l}))^3; \partial u_i / \partial x_i^2 = 0; X^2\text{-periodic}\}$ and $(H^1(\Omega_{2l}))^3$ denotes the Sobolev subspace of the Hilbert space $(L_2(\Omega_{2l}))^3$. Here, we use L_2 -inner product notation $\langle \cdot, \cdot \rangle$ for simplicity:

$$\langle f, g \rangle = \int_{\Omega_2} f(\mathbf{x}^2) g(\mathbf{x}^2) d\mathbf{x}^2.$$

Then setting $w_i = v_i^k$ together with the microscale incompressible condition yields

$$\left\langle -\eta \frac{\partial v_i^k}{\partial x_j^2}, \frac{\partial v_i^k}{\partial x_j^2} \right\rangle + \left\langle \delta_{ki}, v_i^k \right\rangle = 0, \quad (67)$$

which shows the symmetry of v_i^k and eventually the symmetry and the nonnegative definiteness of K_{ji}^k :

$$v_i^k = v_j^i; K_{ji}^k = K_{ij}^k; K_{ij}^k \xi_i \xi_j \geq 0, \quad \forall \xi. \quad (68)$$

Taking the average of Eqn (58) in the microscale domain, we have

$$\begin{aligned} \langle V_i^0 \rangle_2 &= -K_{ji}^k \left(\frac{\partial P^0}{\partial x_j^0} - F_j \right) - \frac{1}{|\Omega_2|} \int_{\Omega_2} \frac{\partial P^1}{\partial x_j^1} v_i^k d\mathbf{x}^2 \\ &= -K_{ji}^k \left(\frac{\partial P^0}{\partial x_j^0} - F_j \right) - \frac{1}{|\Omega_2|} \int_{\Omega_2} P^1 v_i^k n_j ds^2 \\ &\quad + \frac{1}{|\Omega_2|} \int_{\Omega_2} P^1 \frac{\partial v_i^k}{\partial x_j^1} d\mathbf{x}^2. \end{aligned}$$

The second term of the right-hand-side vanishes because of the periodicity of $P^1 v_i^k$, and the last term also vanishes because of the symmetry of v_i^k and the microscale incompressible condition. Thus we have the *mesoscale Darcy's law*:

$$\langle V_i^0 \rangle_2 = -K_{ji}^k \left(\frac{\partial P^0}{\partial x_j^0} - F_j \right). \quad (69)$$

Averaging in the microscale domain for Eqn (63) yields

$$-\frac{\partial}{\partial x_i^0} \left\{ K_{ji}^k \left(\frac{\partial P^0}{\partial x_j^0} - F_j \right) \right\} + \frac{\partial}{\partial x_i^1} \langle V_i^1 \rangle_2 = 0,$$

since the third term of Eqn (63) vanishes due to periodicity in the microscale domain. Furthermore, we introduce an average in the mesoscale domain Ω_1 by $\langle \cdot \rangle_1$ for this equation, and get the *macroscale seepage equation*:

$$-\frac{\partial}{\partial x_i^0} \left\{ K_{ji}^k \left(\frac{\partial P^0}{\partial x_j^0} - F_j \right) \right\} = 0 \quad \text{in } \Omega_0. \quad (70)$$

where the *macroscale homogenized permeability* K_{ji}^k is defined by

$$K_{ji}^k = \left\langle K_{ji}^k \right\rangle_1 = \frac{1}{|\Omega_1|} \int_{\Omega_1} K_{ji}^k d\mathbf{x}^1, \quad (71)$$

and the *macroscale Darcy's law* is given by

$$\tilde{V}_i^0 = \left\langle \left\langle V_i^0 \right\rangle_2 \right\rangle_1 = -K_{ji}^k \left(\frac{\partial P^0}{\partial x_j^0} - F_j \right), \quad (72)$$

where \tilde{V}_i^0 is the average of V_i^0 .

The first order approximations of true pressure P^e and velocity V_i^e are given by

$$V_i^e(\mathbf{x}) \simeq \varepsilon^4 V_i^0(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2), \quad P^e(\mathbf{x}) \simeq P^0(\mathbf{x}^0, \mathbf{x}^1). \quad (73)$$

The total procedure to solve the multiscale HA-seepage problem is summarized as follows. We first solve the microscale equations (60), (64) and get v_i^k and p^k , then determine the mesoscale and macroscale Darcy's coefficients K_{ij}^k and K_{ij} using Eqns (65) and (71), respectively. Next, by solving the macroscale seepage equation (70) we get the macro-pressure P^0 . Substituting these into Eqn (73) we can finally specify the true pressure and velocity fields.

In geotechnical engineering we usually use the following empirical Darcy's law

$$\tilde{V}_i^* = -K_{ij}^* \frac{\partial H}{\partial x_j}; \quad H = \frac{P}{\rho_w g} + \zeta \quad (74)$$

where \tilde{V}_i^* is average seepage velocity, H total head, and ζ elevation head. Comparing this with Eqns (72) and (73), we find the correspondence

$$\tilde{V}_i^* = \langle \langle V_i^0 \rangle_2 \rangle_1 \simeq \varepsilon^4 \tilde{V}_i^0, \quad (75)$$

so we have the following interpretation between the macroscale HA-*permeability* K_{ij} and the conventional permeability (called the C-*permeability*) K_{ij}^* :

$$K_{ij}^* = \varepsilon^4 \rho_w g K_{ij}. \quad (76)$$

where ρ_w the mass density of water, which is assumed to be constant because of incompressibility, and g the gravitational acceleration. True velocity V_i^e is crucially affected by the sizes of mesoscale and microscale structures, while true pressure P^e is not.

4.2 Three-dimensional two-scale homogenization analysis of sand

To justify the homogenization procedure compared to the conventional seepage theory here we present a simple three-dimensional model of quartz sand, because there is no need to consider any significant effect of the interaction between minerals (i. e. quartz) and pore water. A two-scale homogenization method is employed; that is, the coordinate systems are $\mathbf{x}^0, \mathbf{x}^1$ ($\mathbf{x}^1 = \mathbf{x}^0 / \varepsilon$). Instead of the asymptotic expansion (52) we use

$$V_i^e(\mathbf{x}) = \varepsilon^2 V_i^0(\mathbf{x}^0, \mathbf{x}^1) + \varepsilon^3 V_i^1(\mathbf{x}^0, \mathbf{x}^1) + \dots$$

The microscale Stokes' equation is the same as Eqn

(60), together with the microscale incompressible equation (64). The macroscale permeability is given by

$$K_{ij} = \langle v_j^i \rangle = \frac{1}{|\Omega_1|} \int_{\Omega_1} v_j^i d\mathbf{x}^1.$$

The macroscale Darcy's law is the same as Eqn (72), and the first order approximation of velocity is $V_i^j(\mathbf{x}) \approx \varepsilon^2 V_i^j(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2)$, $P^e(\mathbf{x}) \approx P^0(\mathbf{x}^0)$. So compared to C-permeability (74) we have the correspondence

$$K_{ij}^* = \varepsilon^2 \rho_w g K_{ij}.$$

The model is shown in Fig. 4. A unit cell is cubic with the sides X_1 , and sand grains are also assumed to be cubic with the sides d . The void ratio e , the ratio of void part ΔV_v to solid part ΔV_s , i.e., $e = \Delta V_v /$

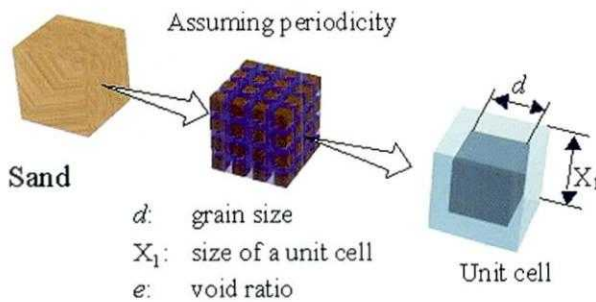


Fig. 4. Assumed microstructure of sand.

ΔV_s , is calculated as

$$e = \frac{X_1^3 - d^3}{d^3}.$$

Based on experiments several empirical equations giving the permeability k ($K_{ij}^* = k\delta_{ij}$) are proposed. Some are as follows:

Hazen's formula: $k = C_K(0.7 + 0.03 T)D_w^2$,

Terzaghi's formula: $k = \frac{C_t}{\eta} \left(\frac{n-0.13}{\sqrt[3]{1-n}} \right)^2 D_{10}^2$,

Zunker's formula: $k = \frac{C_z}{\eta} \left(\frac{n}{1-n} \right)^2 D_w^2$,

Kozeny-Donat's formula: $k = \frac{C_k}{\eta} \left(\frac{n^3}{(1-n)^2} \right)^2 D_w^2$,

where C_K, C_t, C_k are constants depending on characteristics of sand, T temperature, D_w average grain size, D_{10} effective grain size, n porosity, and η viscosity of water. It is noted in all equations that permeability k is proportional to the squares of grain size D_{10} or D_w , and is inversely proportional to viscosity η .

The C-permeability calculated by HA is comparable to the above empirical forms. We give the compared results in Fig. 5 and 6 for the temperatures $T = 10^\circ\text{C}$ and 30°C , respectively. Note that we use the following constants: $C_K = 150$ for the Hazen's formula, $C_t = 6$ for the Terzaghi's formula and $C_k = 2.3$ for

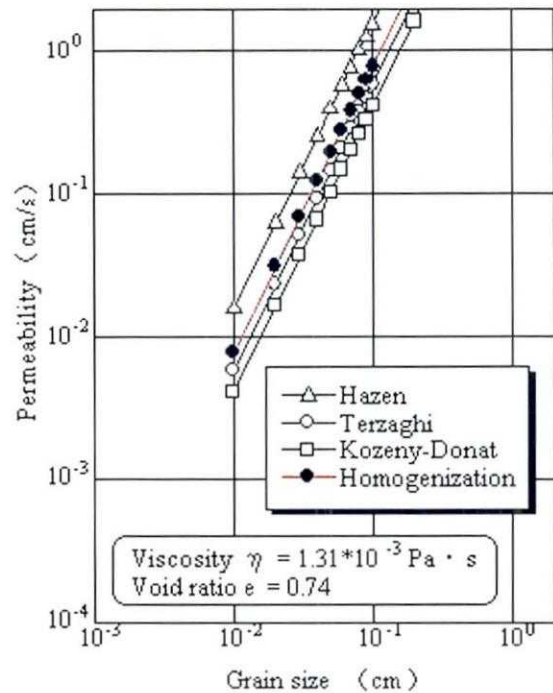
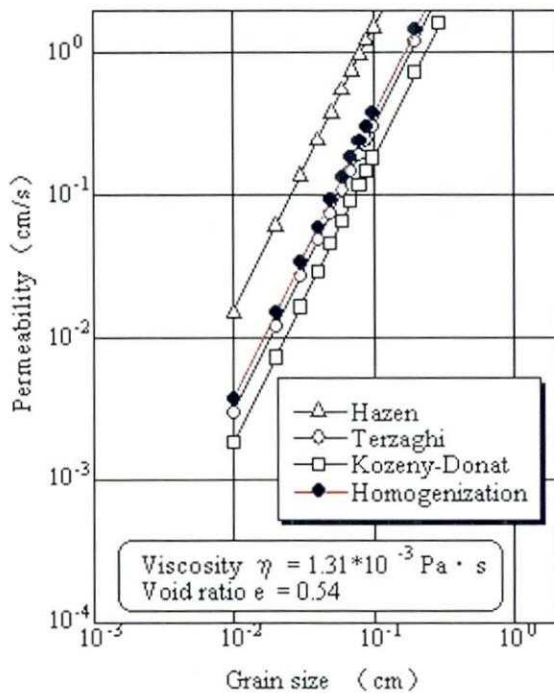


Fig. 5. Permeability for sand at $T = 10^\circ\text{C}$.

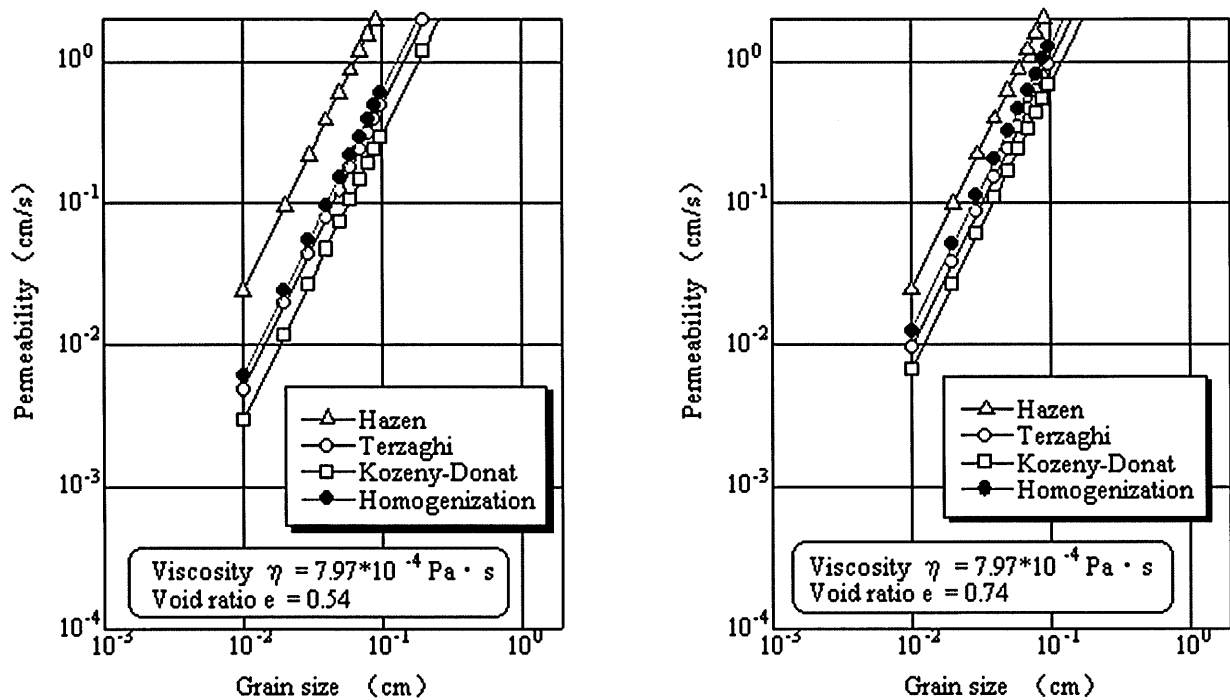

 Fig. 6. Permeability sand at for $T=30^{\circ}\text{C}$.

Table 2. Data for diffusion of plutonium (Pu) in bentonite (JNC 2000).

Diffusion coefficient D_{ij}^e (cm^2/year)	Distribution factor K_d (m^3/kg)	Average dry density (Mg/m^3)
94.6	10.0	1.60

the Kozeny-Donat's formula. We understand that both HA and empirical-based results are quite compatible.

4.3 Two-dimensional three-scale homogenization analysis of bentonite with distributed water viscosity

As mentioned in the section discussing MD simulation, water viscosity changes greatly in the neighborhood of clay minerals. In this case we can solve the microscale equations (60) and (64) using the finite element method. Then we calculate mesoscale permeability K_{ij}^* , macroscale HA-permeability K_{ij} , and C-permeability K_{ij}^* .

The target bentonite, Kunigel V1, consists of about 50% of montmorillonite in weight and the rest of macro-grains, mainly quartz particles. The mass density of a crystal is $2.7\text{ g}/\text{cm}^3$, both for montmorillonite and for quartz, so one third ($1/3$) of the bentonite with its dry density $1.8\text{ g}/\text{cm}^3$ is void (i.e., the

void ratio $e=0.5$). Based on a measurement of the sizes of macro-grains, we understand sizes vary widely from 5 to $100\mu\text{m}$ in diameter. Considering the peak value of this grain-size curve and taking into account the fact that permeability is affected by smaller particles, we set the size of macro-grains as $15\mu\text{m}$ and the size of a meso-domain as $45\mu\text{m}$ (three times of the grain size). On the other hand, the size of one montmorillonite lamellar crystal is about $100 \times 100 \times 1\text{ nm}$, and several parallel lamellae together form a group, which we call a *lamellae group*. Here we assume a group of six lamellae with an interlayer distance of 0.56 nm corresponding to two-layers of hydrated water molecules, and this is set as one of the micro-scale domains. Since the width is much larger than the thickness, the domain in local x_2^2 direction is set to be infinite. The inter-group distance X of Fig. 7 is determined by the given saturated density. If this X becomes smaller than 0.56 nm ,

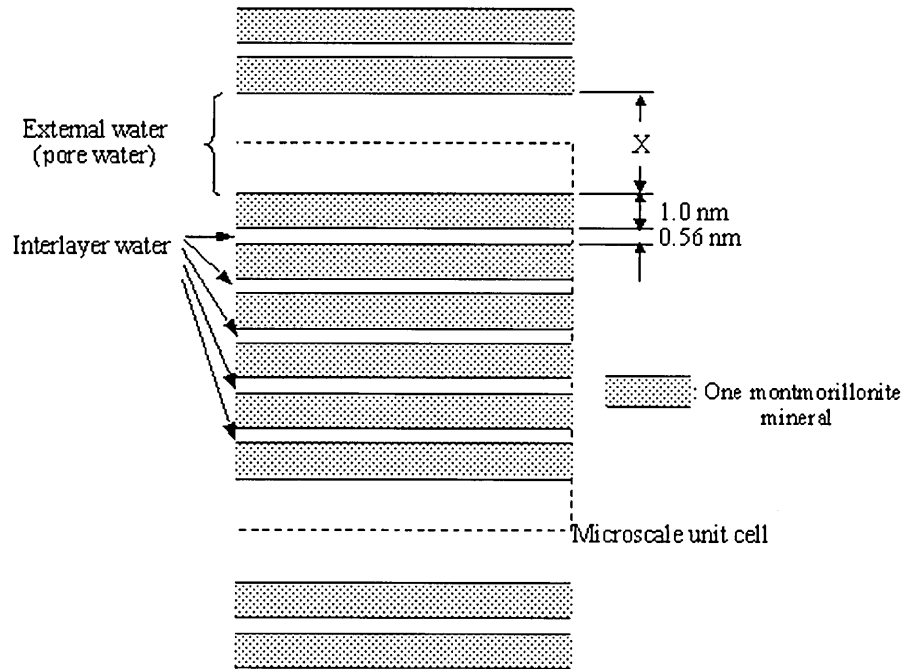


Fig. 7. Microscale unit cell for clay hydrate (corresponding to the microscale problem 1 of Fig. 3).

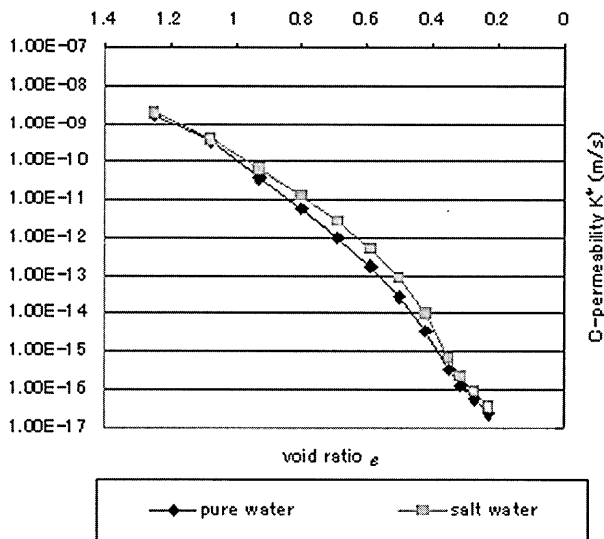


Fig. 8. C-permeability of Kunigel V1 saturated with pure- and salt-water.

the inter-lamellae distance is set to be the same as X . The local value of viscosity for pure- and salt-water is obtained by MD (Fig. 2). Note that after calculating K_1^2 of Eqn (65) using this pseudo-one dimensional model, we set the homogeneous K^2 to be $K^2 = K_{11}^2/3$, because of the random distribution of lamellae groups. Another micro-domain is of a quartz grain, which is completely impermeable. Under these con-

ditions we calculate C-permeability, and the results are shown in Fig. 8. We understand that permeability varies greatly due to changes of the void ratio e .

5. Multiscale homogenization theory for diffusion problem in porous media

As mentioned in the procedure for deriving diffusion equation (44) or (46), the adsorption phenomenon is evaluated as an alternative form of the concentration in the solid phase and the (linear) adsorption isotherm (43). This involves difficulties in interpreting the adsorption phenomenon in a physically and chemically true manner. We present a new procedure for solving the difficulties by extending the micro-characteristics to macro-behavior through the coupled molecular dynamics (MD) and homogenization analysis (HA) method. Here the microscopic properties are calculated by MD, and HA is used to analyze micro-/macro-behavior.

5.1 Governing equation of diffusion problem

We treat the diffusion problem of a multicomponent solution in an undeformable solid skeleton. In this HA we need to think only of the flow region, so referring to Eqn(13) the starting mass conservation law can be given as

$$\int_{\Omega_f} \left[\frac{\partial(\rho c_\alpha)}{\partial t} + \frac{\partial}{\partial x_i} (\rho c_\alpha v_i^\alpha) + \dot{\gamma}_\alpha \right] dv - \int_{\Gamma_{fs}} \xi_i^\alpha n_i ds = 0 \quad (77)$$

where c_α is mass-percent concentration of the α -th component, ρ average mass density of solution given by Eqn(6), \mathbf{v}^α particle velocity of the α -th component, $\dot{\gamma}_\alpha$ source term of the α -th component due to chemical reaction, *etc.*, Ω_f flow region, Γ_{fs} internal fluid-solid interface, ζ_i^α mass flux of the α -th component on Γ_{fs} adsorbed from the solution, and n_i unit outward normal.

The average velocity of solution, \mathbf{v} , and the diffusing mass flux of the α -th component, \mathbf{j}^α , are defined in the same was as in Eqns(16) and (17):

$$\mathbf{v} = \frac{1}{\rho} \sum_{\alpha=1}^n \rho_\alpha \mathbf{v}^\alpha = \sum_{\alpha=1}^n c_\alpha \mathbf{v}^\alpha, \quad \mathbf{j}^\alpha = \rho_\alpha (\mathbf{v}^\alpha - \mathbf{v}) = \rho c_\alpha (\mathbf{v}^\alpha - \mathbf{v}). \quad (78)$$

We apply the divergence theorem to the last term of LHS of Eqn (77), in which we note that the flux boundary Γ_f consists of an outer one Γ_{of} and an internal fluid-solid interface Γ_{sf} , but on the outer boundary Γ_{of} we have no adsorption:

$$\int_{\Gamma_{fs}} \zeta_i^\alpha n_i ds = \int_{\Omega_f} \frac{\partial \zeta_i^\alpha}{\partial x_i} dv - \int_{\Gamma_{of}} \zeta_i^\alpha n_i ds = \int_{\Omega_f} \frac{\partial \zeta_i^\alpha}{\partial x_i} dv.$$

And, we apply Fick's first law (19) to the second term of LHS of Eqn(77), then the following diffusion equation is obtained:

$$\begin{aligned} \frac{\partial(\rho c_\alpha)}{\partial t} + v_i \frac{\partial(\rho c_\alpha)}{\partial x_i} - \frac{\partial}{\partial x_i} \left(\sum_{\beta=1}^n \rho D_{\alpha\beta} \frac{\partial c_\beta}{\partial x_i} \right) \\ + \dot{\gamma}_\alpha - \frac{\partial \zeta_i^\alpha}{\partial x_i} = 0. \end{aligned} \quad (79)$$

For simplicity we henceforth the micro-/macro-diffusion problem of one chemical species ($\alpha=1$), so we set $c^\varepsilon = c_\alpha$ and $\rho f^\varepsilon = \dot{\gamma}_\alpha - \partial \zeta_i^\alpha$. Here the superscript ε implies field variables that rapidly fluctuate. Then under the incompressible condition of the solution ($\rho = \text{constant}$, $\partial v_i^\varepsilon / \partial x_i = 0$) we have the following system of partial differential equations:

Governing equation;

$$\frac{\partial c^\varepsilon}{\partial t} + v_j^\varepsilon \frac{\partial c^\varepsilon}{\partial x_j} - \frac{\partial}{\partial x_i} \left(D_{ij}^\varepsilon \frac{\partial c^\varepsilon}{\partial x_j} \right) + f^\varepsilon = 0 \text{ in } \Omega_f, \quad (80)$$

Boundary conditions;

$$\text{(Dirichlet condition); } c^\varepsilon(\mathbf{x}, t) = \hat{c}^\varepsilon(t) \text{ on } \partial\Omega_c \quad (81)$$

$$\text{(Neumann condition); } -D_{ij}^\varepsilon \frac{\partial c^\varepsilon}{\partial x_j} n_i = \hat{q}(t) \text{ on } \partial\Omega_q \quad (82)$$

Initial condition;

$$c^\varepsilon(\mathbf{x}, t) = c_0^\varepsilon(\mathbf{x}) \text{ at } t = t_0 \quad (83)$$

5.2 Micro-, meso-, and macro-scale equations

We introduce a perturbation for the global concentration function $c^\varepsilon(\mathbf{x}; t)$ with respect to the macro-, meso-, and micro-coordinate systems \mathbf{x}^0 , \mathbf{x}^1 and \mathbf{x}^2 ,

respectively, as follows:

$$c^\varepsilon(\mathbf{x}; t) = c^0(\mathbf{x}^0; t) + \varepsilon c^1(\mathbf{x}^0, \mathbf{x}^1; t) + \dots; \quad (84)$$

$$\mathbf{x}^1 = \frac{\mathbf{x}^0}{\varepsilon}, \quad \mathbf{x}^2 = \frac{\mathbf{x}^1}{\varepsilon}$$

where c^α s ($\alpha=0, 1, 2, \dots$) are X^1 -/ X^2 -periodic functions:

$$c^\alpha(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2; t) = c^\alpha(\mathbf{x}^0, \mathbf{x}^1 + X^1, \mathbf{x}^2; t),$$

$$c^\alpha(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2; t) = c^\alpha(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2 + X^2; t).$$

As given by Eqn (50) differentiation with respect to \mathbf{x} can be written by the terms of \mathbf{x}^0 , \mathbf{x}^1 , and \mathbf{x}^2 :

$$\frac{\partial}{\partial x_i} = \frac{\partial}{\partial x_i^0} + \frac{1}{\varepsilon} \frac{\partial}{\partial x_i^1} + \frac{1}{\varepsilon^2} \frac{\partial}{\partial x_i^2}$$

Thus the differentiation for the global concentration function c^ε becomes

$$\begin{aligned} \frac{\partial c^\varepsilon}{\partial x_j} = \varepsilon^{-2} \frac{\partial c^0}{\partial x_j^2} + \varepsilon^{-1} \left(\frac{\partial c^0}{\partial x_j^1} + \frac{\partial c^1}{\partial x_j^2} \right) \\ + \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} + \frac{\partial c^2}{\partial x_j^2} \right) + \varepsilon(\dots) + \dots. \end{aligned} \quad (85)$$

The governing equation (80) is then perturbed as

$$\begin{aligned} \left(\frac{\partial c^0}{\partial t} + \varepsilon \frac{\partial c^1}{\partial t} + \varepsilon^2 \frac{\partial c^2}{\partial t} + \dots \right) \\ + \left[\varepsilon^{-2} v_j^\varepsilon \frac{\partial c^0}{\partial x_j^2} + \varepsilon^{-1} v_j^\varepsilon \left(\frac{\partial c^0}{\partial x_j^1} + \frac{\partial c^1}{\partial x_j^2} \right) \right. \\ \left. + v_j^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} + \frac{\partial c^2}{\partial x_j^2} \right) + \dots \right] \\ - \left[\varepsilon^{-4} \left\{ \frac{\partial}{\partial x_i^2} \left(D_{ij}^\varepsilon \frac{\partial c^0}{\partial x_j^2} \right) \right\} + \varepsilon^{-3} \left\{ \frac{\partial}{\partial x_i^1} \left(D_{ij}^\varepsilon \frac{\partial c^0}{\partial x_j^2} \right) \right. \right. \\ \left. \left. + \frac{\partial}{\partial x_i^2} \left(D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^1} + \frac{\partial c^1}{\partial x_j^2} \right) \right) \right\} \right. \\ \left. + \varepsilon^{-2} \left\{ \frac{\partial}{\partial x_i^0} \left(D_{ij}^\varepsilon \frac{\partial c^0}{\partial x_j^2} \right) + \frac{\partial}{\partial x_i^1} \left(D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^1} + \frac{\partial c^1}{\partial x_j^2} \right) \right) \right. \right. \\ \left. \left. + \frac{\partial}{\partial x_i^2} \left(D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} + \frac{\partial c^2}{\partial x_j^2} \right) \right) \right\} \right. \\ \left. + \varepsilon^{-1} \left\{ \frac{\partial}{\partial x_i^0} \left(D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^1} + \frac{\partial c^1}{\partial x_j^2} \right) \right) \right. \right. \\ \left. \left. + \frac{\partial}{\partial x_i^1} \left(D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} + \frac{\partial c^2}{\partial x_j^2} \right) \right) \right. \right. \\ \left. \left. + \frac{\partial}{\partial x_i^2} \left(D_{ij}^\varepsilon \left(\frac{\partial c^1}{\partial x_j^0} + \frac{\partial c^2}{\partial x_j^1} + \frac{\partial c^3}{\partial x_j^2} \right) \right) \right\} \right. \\ \left. + \left\{ \frac{\partial}{\partial x_i^0} \left(D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} + \frac{\partial c^2}{\partial x_j^2} \right) \right) \right. \right. \\ \left. \left. + \frac{\partial}{\partial x_i^1} \left(D_{ij}^\varepsilon \left(\frac{\partial c^1}{\partial x_j^0} + \frac{\partial c^2}{\partial x_j^1} + \frac{\partial c^3}{\partial x_j^2} \right) \right) \right. \right. \\ \left. \left. + \frac{\partial}{\partial x_i^2} \left(D_{ij}^\varepsilon \left(\frac{\partial c^2}{\partial x_j^0} + \frac{\partial c^3}{\partial x_j^1} + \frac{\partial c^4}{\partial x_j^2} \right) \right) \right\} \right. \\ \left. + \varepsilon \{ \cdot \} + \dots \right] + f^\varepsilon = 0, \end{aligned}$$

and we get the following partial differential equations corresponding to each ε -term.

$O(\varepsilon^{-4})$ -term:

$$\frac{\partial}{\partial x_i^2} \left(D_{ij}^\varepsilon \frac{\partial c^0}{\partial x_j^2} \right) = 0.$$

Since c^0 is a function only of \mathbf{x}^0 , this is automatically satisfied.

$O(\varepsilon^{-3})$ -term: First characteristic function

$$\frac{\partial}{\partial x_i^1} \left(D_{ij}^\varepsilon \frac{\partial c^0}{\partial x_j^2} \right) + \frac{\partial}{\partial x_i^2} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^1} + \frac{\partial c^1}{\partial x_j^2} \right) \right\} = 0.$$

The terms $\partial c^0 / \partial x_j^2$ and $\partial c^0 / \partial x_j^1$ vanish, so c^1 is independent from \mathbf{x}^2 , which suggests the existence of the *first characteristic function* $N_k^1(\mathbf{x}^1)$ such as

$$c^1 = c^1(\mathbf{x}^0, \mathbf{x}^1; t) = -N_k^1(\mathbf{x}^1) \frac{\partial c^0(\mathbf{x}^0; t)}{\partial x_k^0} + \bar{c}^1(\mathbf{x}^0; t) \quad (86)$$

where $\bar{c}^0(\mathbf{x}^0; t)$ is an integration constant.

$O(\varepsilon^{-2})$ -term: Second characteristic function and microscale equation [MiSE]

$$\begin{aligned} v_j^\varepsilon \frac{\partial c^0}{\partial x_j^2} - \frac{\partial}{\partial x_i^0} \left(D_{ij}^\varepsilon \frac{\partial c^0}{\partial x_j^2} \right) - \frac{\partial}{\partial x_i^1} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^1} + \frac{\partial c^1}{\partial x_j^2} \right) \right\} \\ - \frac{\partial}{\partial x_i^2} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} + \frac{\partial c^2}{\partial x_j^2} \right) \right\} = 0. \end{aligned}$$

The first three terms vanish, so we have the following local equation:

$$\frac{\partial}{\partial x_i^2} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} + \frac{\partial c^2}{\partial x_j^2} \right) \right\} = 0. \quad (87)$$

Since the term $\partial c^0 / \partial x_j^0 + \partial c^1 / \partial x_j^1$ is a function only of \mathbf{x}^0 and \mathbf{x}^1 , we have the *second characteristic function* $N_k^2(\mathbf{x}^2)$ such as

$$\begin{aligned} c^2(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2; t) = -N_k^2(\mathbf{x}^2) \left(\frac{\partial c^0}{\partial x_k^0} + \frac{\partial c^1}{\partial x_k^1} \right) \\ + \bar{c}^2(\mathbf{x}^0, \mathbf{x}^1; t) = -N_k^2 \left(\delta_{kl} - \frac{\partial N_l^1}{\partial x_k^1} \right) \frac{\partial c^0}{\partial x_l^0} + \bar{c}^2. \end{aligned} \quad (88)$$

Here Eqn (86) is used. Then we have

$$\begin{aligned} D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} + \frac{\partial c^2}{\partial x_j^2} \right) \\ = D_{ij}^\varepsilon \left(\delta_{jk} - \frac{\partial N_k^2}{\partial x_j^2} \right) \left(\delta_{kl} - \frac{\partial N_l^1}{\partial x_k^1} \right) \frac{\partial c^0}{\partial x_l^0} \end{aligned} \quad (89)$$

Substituting this into Eqn (87) yields the following *microscale equation* [MiSE], together with X^2 -periodic boundary condition for the microscale domain Ω_2 :

$$\frac{\partial}{\partial x_i^2} \left\{ D_{ij}^\varepsilon \left(\delta_{jk} - \frac{\partial N_k^2}{\partial x_j^2} \right) \right\} = 0 \quad \text{in } \Omega_2. \quad (90)$$

$O(\varepsilon^{-1})$ -term: Mesoscale equation [MeSE]

$$\begin{aligned} v_j^\varepsilon \left(\frac{\partial c^0}{\partial x_j^1} + \frac{\partial c^1}{\partial x_j^2} \right) - \frac{\partial}{\partial x_i^0} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^1} + \frac{\partial c^1}{\partial x_j^2} \right) \right\} \\ - \frac{\partial}{\partial x_i^1} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} + \frac{\partial c^2}{\partial x_j^2} \right) \right\} \\ - \frac{\partial}{\partial x_i^2} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^1}{\partial x_j^0} + \frac{\partial c^2}{\partial x_j^1} + \frac{\partial c^3}{\partial x_j^2} \right) \right\} = 0. \end{aligned}$$

The first two terms vanish, so we have

$$\begin{aligned} \frac{\partial}{\partial x_i^1} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} + \frac{\partial c^2}{\partial x_j^2} \right) \right\} \\ + \frac{\partial}{\partial x_i^2} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^1}{\partial x_j^0} + \frac{\partial c^2}{\partial x_j^1} + \frac{\partial c^3}{\partial x_j^2} \right) \right\} = 0. \end{aligned} \quad (91)$$

We introduce the volume average $\langle \cdot \rangle_2$ of the microscale domain Ω_2 , then the last term vanishes because of X^2 -periodicity. Substituting Eqn (89) into this we finally get the *mesoscale equation* [MeSE] together with X^1 -periodic boundary condition for the mesoscale domain Ω_1 :

$$\frac{\partial}{\partial x_i^1} \left\{ D_{ik}^{H_2} \left(\delta_{kl} - \frac{\partial N_l^1}{\partial x_k^1} \right) \right\} = 0 \quad \text{in } \Omega_1 \quad (92)$$

$$D_{ik}^{H_2} = \frac{1}{|\Omega_2|} \int_{\Omega_2} D_{ij}^\varepsilon \left(\delta_{jk} - \frac{\partial N_k^2}{\partial x_j^2} \right) d\mathbf{x}^2. \quad (93)$$

$O(\varepsilon^0)$ -term: Macro-scale equation [MaSE]

$$\begin{aligned} \frac{\partial c^0}{\partial t} + v_j^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} + \frac{\partial c^2}{\partial x_j^2} \right) \\ - \frac{\partial}{\partial x_i^0} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} + \frac{\partial c^2}{\partial x_j^2} \right) \right\} \\ - \frac{\partial}{\partial x_i^1} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^1}{\partial x_j^0} + \frac{\partial c^2}{\partial x_j^1} + \frac{\partial c^3}{\partial x_j^2} \right) \right\} \\ - \frac{\partial}{\partial x_i^2} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^2}{\partial x_j^0} + \frac{\partial c^3}{\partial x_j^1} + \frac{\partial c^4}{\partial x_j^2} \right) \right\} + f^\varepsilon = 0. \end{aligned} \quad (94)$$

We substitute Eqn (89) into this and make the average for the microscale domain Ω_2 :

$$\begin{aligned} \frac{\partial c^0}{\partial t} + v_k^{H_2} \left(\delta_{kl} - \frac{\partial N_l^1}{\partial x_k^1} \right) \frac{\partial c^0}{\partial x_l^0} - \frac{\partial}{\partial x_i^0} \left\{ D_{ik}^{H_2} \left(\delta_{kl} - \frac{\partial N_l^1}{\partial x_k^1} \right) \frac{\partial c^0}{\partial x_l^0} \right\} \\ - \frac{\partial}{\partial x_i^1} \left\{ D_{ij}^\varepsilon \left(\frac{\partial c^1}{\partial x_j^0} + \frac{\partial c^2}{\partial x_j^1} + \frac{\partial c^3}{\partial x_j^2} \right) \right\} + f^{H_2} = 0, \end{aligned}$$

where

$$\begin{aligned} v_k^{H_2} = \frac{1}{|\Omega_2|} \int_{\Omega_2} v_j^\varepsilon \left(\delta_{jk} - \frac{\partial N_k^2}{\partial x_j^2} \right) d\mathbf{x}^2, \\ f^{H_2} = \frac{1}{|\Omega_2|} \int_{\Omega_2} f^\varepsilon d\mathbf{x}^2. \end{aligned} \quad (95)$$

We again make average for the mesoscale domain Ω_1 to get the *macroscale equation* [MaSE]:

$$\frac{\partial c^0}{\partial t} + v_i^{H_1} \frac{\partial c^0}{\partial x_i^0} - \frac{\partial}{\partial x_i^0} \left(D_{il}^{H_1} \frac{\partial c^0}{\partial x_l^0} \right) + f^{H_1} = 0 \quad \text{in } \Omega_0 \quad (96)$$

where

$$\begin{aligned} v_i^{H_1} = \frac{1}{|\Omega_1|} \int_{\Omega_1} v_k^{H_2} \left(\delta_{kl} - \frac{\partial N_l^1}{\partial x_k^1} \right) d\mathbf{x}^1, \\ D_{il}^{H_1} = \frac{1}{|\Omega_1|} \int_{\Omega_1} D_{ik}^{H_2} \left(\delta_{kl} - \frac{\partial N_l^1}{\partial x_k^1} \right) d\mathbf{x}^1, \\ f^{H_1} = \frac{1}{|\Omega_1|} \int_{\Omega_1} f^{H_2} d\mathbf{x}^1. \end{aligned} \quad (97)$$

The macroscale equation [MaSE] can be solved together with the boundary conditions (81) and (82) and the initial condition (83).

Table 3. Calculated and experimental effective diffusion coefficient of HTO in saturated bentonite with its dry density 2.0 g/cm³ (experiment, JNC 2000).

	Effective diffusion coefficient of HTO (cm ² /year)	
	Calculated (multiscale HA)	Experiment
8-layer model	28.384	16.083
6-layer model	20.892	
4-layer model	16.068	

The procedure to solve the multiscale diffusion problem is summarized as follows:

- 1) Calculate the second characteristic function N_2^k by solving MiSE (90) under the X^2 -periodic boundary condition.
- 2) Determine mesoscale diffusivity $D_{ik}^{H_2}$ by Eqn (93), then calculate the first characteristic function N_1^l by solving MeSE (92) under the X^1 -periodic boundary condition.
- 3) Determine mesoscale velocity $v_k^{H_2}$ and mesoscale source term f^{H_2} using Eqn (95).
- 4) Determine macroscale diffusivity D_{il}^H , macroscale velocity v^H and macroscale source term f^H using Eqn (97), then calculate c^0 by solving MaSE (94) under the boundary conditions (81) and (82) and the initial condition (83).
- 5) The true concentration c^ε calculated as

$$\begin{aligned}
 c^\varepsilon(\mathbf{x}; t) &\simeq c^0(\mathbf{x}^0; t) + \varepsilon c^1(\mathbf{x}^0, \mathbf{x}^1; t) \\
 &\quad + \varepsilon^2 c^2(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2; t) \\
 &= c^0 - \varepsilon \left\{ N_1^l + \varepsilon N_2^k \left(\delta_{kl} - \frac{\partial N_1^l}{\partial x_k^0} \right) \right\} \frac{\partial c^0}{\partial x_l^0}.
 \end{aligned} \tag{98}$$

5.3 Diffusion of tritium water HTO in bentonite

Tritium water $^3\text{H}_2\text{O}$, denoted simply as HTO, is non-adsorptive, so it is appropriate to check the applicability of our analysis. The diffusion coefficient of HTO in free water is reported as $2.44 \times 10^{-5} \text{ cm}^2/\text{s} = 769.48 \text{ cm}^2/\text{year}$ (Klitzsche *et al.* 1976). Using the same microscale lamellae model given by Fig. 7 and the mesoscale model with quartz particles of the size 15 μm , we calculate the effective diffusivity, which is equivalent to the macroscale diffusivity D^H . Note that we here change the number of lamellae as 8, 6, and 4 under fixed dry density 2.0 g/cm³. As mentioned in the seepage calculation, the microscale model is pseudo-one-dimensional, so we set the homogeneous D^H to be $D^H = D_{11}^H/3$. Furthermore, we assume that in the neighborhood of the clay surface the diffusion coefficient D^ε of HTO varies in the same profile as the normal water shown in Fig. 2, since the chemical properties of tritium water HTO are same

as the normal water.

Results corresponding to 8, 6, and 4 layers are given in Table 3, together with an experimental one. We can say that the 4-layer model gives a very compatible result to the experimental one. However, here we do not account for the geometrical tortuosity effect, so the 6-layer model is not bad.

5.4 Higher order extension including microscale adsorption

If we study the problem including microscale adsorption, the local source term strictly affects the local concentration distribution, in which we need to consider higher terms.

Let us consider the weak form of Eqn (91) in the microscale domain together with X^2 -periodicity

$$\begin{aligned}
 &\left\langle D_{ij}^\varepsilon \left(\delta_{jk} - \frac{\partial N_2^k}{\partial x_j^0} \right) \frac{\partial^2 N_1^l}{\partial x_l^0 \partial x_k^0 \partial x_l^0} \frac{\partial c^0}{\partial x_l^0}, w \right\rangle \\
 &+ \left\langle D_{ij}^\varepsilon \left(-N_1^k \frac{\partial^2 c^0}{\partial x_j^0 \partial x_k^0} + N_2^k \frac{\partial^2 N_1^l}{\partial x_l^0 \partial x_k^0} \frac{\partial c^0}{\partial x_l^0} + \frac{\partial c^3}{\partial x_j^2} \right), \frac{\partial w}{\partial x_l^0} \right\rangle \\
 &= 0 \quad \forall w \in V_{x^2}
 \end{aligned} \tag{99}$$

where

$$V_{x^2} = \{w \in H^1(\Omega_{2f}); X^2\text{-periodic}\}.$$

We assume D_{ij}^ε is a piece-wise constant in Ω_2 ($D_{ij}^\varepsilon(\mathbf{x}^2)$). The above weak form suggests that c^3 has the following form:

$$\begin{aligned}
 c^3(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2; t) &= N_{31}^k(\mathbf{x}^2) \frac{\partial^2 N_1^m}{\partial x_k^0 \partial x_l^0} \frac{\partial c^0}{\partial x_m^0} \\
 &\quad + N_{32}^k(\mathbf{x}^2) N_1^l(\mathbf{x}^1) \frac{\partial^2 c^0}{\partial x_l^0 \partial x_k^0} + \bar{c}^3(\mathbf{x}^0, \mathbf{x}^1; t)
 \end{aligned} \tag{100}$$

where $N_{31}^k(\mathbf{x}^2)$ and $N_{32}^k(\mathbf{x}^2)$ are characteristic functions. We substitute this into Eqn (99). The terms

$$\frac{\partial^2 N_1^m}{\partial x_k^0 \partial x_l^0} \frac{\partial c^0}{\partial x_m^0}, \quad N_1^l(\mathbf{x}^1) \frac{\partial^2 c^0}{\partial x_l^0 \partial x_k^0}$$

are constant and arbitrary in the domain Ω_2 we get a set of weak equations to specify the characteristic functions:

$$\left\langle D_{ij}^\varepsilon \frac{\partial N_{31}^k}{\partial x_j^0}, \frac{\partial w}{\partial x_l^0} \right\rangle = - \left\langle D_{ik}^\varepsilon N_2^l, \frac{\partial w}{\partial x_l^0} \right\rangle$$

$$\begin{aligned}
 & - \left\langle D_{kj}^{\varepsilon} \left(\delta_{jl} - \frac{\partial N_{32}^k}{\partial x_j^2} \right), w \right\rangle \\
 & \left\langle D_{ij}^{\varepsilon} \frac{\partial N_{32}^k}{\partial x_j^2}, \frac{\partial w}{\partial x_i^2} \right\rangle = \left\langle D_{ik}^{\varepsilon}, \frac{\partial w}{\partial x_i^2} \right\rangle. \quad (101)
 \end{aligned}$$

On the other hand we have the weak form of Eqn (94) as follows:

$$\begin{aligned}
 & \left\langle \frac{\partial c^0}{\partial t} + v_j^{\varepsilon} \left(\delta_{jk} - \frac{\partial N_{32}^k}{\partial x_j^2} \right) \left(\delta_{kl} - \frac{\partial N_{32}^l}{\partial x_k^2} \right) \frac{\partial c^0}{\partial x_l^0}, w \right\rangle \\
 & - \left\langle D_{ij}^{\varepsilon} \left(\delta_{jk} - \frac{\partial N_{32}^k}{\partial x_j^2} \right) \left(\delta_{kl} - \frac{\partial N_{32}^l}{\partial x_k^2} \right) \frac{\partial^2 c^0}{\partial x_i^0 \partial x_l^0}, w \right\rangle \\
 & - \left\langle D_{ij}^{\varepsilon} \left(- \frac{\partial N_{32}^k}{\partial x_i^0} \frac{\partial^2 c^0}{\partial x_j^0 \partial x_k^0} + N_{32}^k \frac{\partial^3 N_{32}^l}{\partial x_i^0 \partial x_j^0 \partial x_k^0} \frac{\partial c^0}{\partial x_l^0} \right. \right. \\
 & \quad \left. \left. + \frac{\partial^2 c^3}{\partial x_i^0 \partial x_j^0} \right), w \right\rangle \\
 & + D_{ij}^{\varepsilon} \left\{ - N_{32}^k \left(\delta_{kl} - \frac{\partial N_{32}^l}{\partial x_k^2} \right) \frac{\partial^2 c^0}{\partial x_j^0 \partial x_l^0} + \frac{\partial c^3}{\partial x_j^0} + \frac{\partial c^4}{\partial x_j^2} \right\}, \frac{\partial w}{\partial x_i^2} \right\rangle \\
 & = 0 \quad \forall w \in V_{x^2}. \quad (102)
 \end{aligned}$$

This weak form suggests that c^4 has the following form:

$$\begin{aligned}
 c^4(\mathbf{x}^0, \mathbf{x}^1, \mathbf{x}^2; t) &= N_{41}^{klm}(\mathbf{x}^2) \frac{\partial^3 N_{32}^m}{\partial x_k^0 \partial x_l^0 \partial x_m^0} \frac{\partial c^0}{\partial x_n^0} \\
 & + N_{42}^{kl}(\mathbf{x}^2) \frac{\partial N_{32}^m}{\partial x_k^0} \frac{\partial^2 c^0}{\partial x_m^0 \partial x_l^0} + N_{43}^{kl}(\mathbf{x}^2) \frac{\partial^2 c^0}{\partial x_k^0 \partial x_l^0} \\
 & + N_{44}^{kl}(\mathbf{x}^2) \left(\delta_{kl} - \frac{\partial N_{32}^l}{\partial x_k^2} \right) \frac{\partial c^0}{\partial x_l^0} + N_{45}(\mathbf{x}^2) \frac{\partial c^0}{\partial t} \\
 & + N_{46}(\mathbf{x}^2; t) + \bar{c}^4(\mathbf{x}^0, \mathbf{x}^1; t) \quad (103)
 \end{aligned}$$

where $N_{41}^{klm}(\mathbf{x}^2), \dots, N_{46}^{kl}(\mathbf{x}^2)$ are characteristic functions. We substitute this into Eqn (102). Since the terms concerning \mathbf{x}^0 and \mathbf{x}^1 are constant and arbitrary in the domain Ω_2 we get a set of weak equations to specify the characteristic functions:

$$\begin{aligned}
 & \left\langle D_{ij}^{\varepsilon} \frac{\partial N_{41}^{klm}}{\partial x_j^2}, \frac{\partial w}{\partial x_i^2} \right\rangle = - \left\langle D_{im}^{\varepsilon} N_{31}^{kl}, \frac{\partial w}{\partial x_i^2} \right\rangle \\
 & + \left\langle D_{mj}^{\varepsilon} \left(N_{32}^k \delta_{ij} + \frac{\partial N_{31}^{kl}}{\partial x_j^2} \right), w \right\rangle \\
 & \left\langle D_{ij}^{\varepsilon} \frac{\partial N_{42}^{kl}}{\partial x_j^2}, \frac{\partial w}{\partial x_i^2} \right\rangle = - \left\langle D_{ik}^{\varepsilon} N_{32}^l + D_{il}^{\varepsilon} N_{32}^k, \frac{\partial w}{\partial x_i^2} \right\rangle \\
 & - \left\langle D_{kj}^{\varepsilon} \left(\delta_{ij} - \frac{\partial N_{32}^l}{\partial x_j^2} \right) + D_{ij}^{\varepsilon} \left(\delta_{jk} - \frac{\partial N_{32}^k}{\partial x_j^2} \right), w \right\rangle \\
 & \left\langle D_{ij}^{\varepsilon} \frac{\partial N_{43}^{kl}}{\partial x_j^2}, \frac{\partial w}{\partial x_i^2} \right\rangle = \left\langle D_{il}^{\varepsilon} N_{32}^k, \frac{\partial w}{\partial x_i^2} \right\rangle \\
 & + \left\langle D_{ij}^{\varepsilon} \left(\delta_{jk} - \frac{\partial N_{32}^k}{\partial x_j^2} \right), w \right\rangle \\
 & \left\langle D_{ij}^{\varepsilon} \frac{\partial N_{44}^{kl}}{\partial x_j^2}, \frac{\partial w}{\partial x_i^2} \right\rangle = - \left\langle v_j^{\varepsilon} \left(\delta_{jk} - \frac{\partial N_{32}^k}{\partial x_j^2} \right), w \right\rangle \\
 & \left\langle D_{ij}^{\varepsilon} \frac{\partial N_{45}}{\partial x_j^2}, \frac{\partial w}{\partial x_i^2} \right\rangle = \left\langle 1, w \right\rangle
 \end{aligned}$$

$$\left\langle D_{ij}^{\varepsilon} \frac{\partial N_{46}}{\partial x_j^2}, \frac{\partial w}{\partial x_i^2} \right\rangle = - \left\langle f^{\varepsilon}, w \right\rangle \quad (104)$$

6. Conclusions

Here we presented a scheme combining molecular behavior and macro-continuum phenomenon for bentonite clay, which is a micro-inhomogeneous material on a nanometer scale.

In Section 2 we summarized the classical diffusion models for soil, and showed many empirical parameters in the phenomenological theory.

In Section 3 we gave the results of a molecular dynamics (MD) simulation for clay hydrate, and showed that in the neighborhood of clay surface water molecules are restricted in their movements. The diffusivity and the viscosity distribution in the neighborhood of clay surface are given in Fig. 2. It is almost impossible to specify these small-scale distributions of material properties by an experimental method.

In Section 4 we introduced a multiscale homogenization analysis (HA) method to derive a seepage flow equation in porous media with micro-meso-macro-scale structures, starting with the fundamental Stokes equation. It is important that in our analysis we can specify the actual velocity field, even for a material with very irregularly shaped micro-structures. In Fig. 4 we showed that our analysis is consistent with the classical experiment-based seepage theory for a simple quartz sand, in which the water viscosity is constant in the whole fluid region. Next, we calculated the permeability of bentonite clay by applying a three-scale HA model, in which we used the MD results of water viscosity distribution (Fig. 2). It is shown that permeability is greatly reduced as the void part is decreased.

In Section 5 we introduced a multiscale diffusion analysis in porous media that involves a new type of adsorption model. The diffusion properties calculated by MD are also introduced. A macroscopic diffusion property (i.e., effective diffusion coefficient) of tritium water in bentonite is calculated by the proposed method, which gives a result that is reasonably compatible with experimental data (Table 3).

It is well-known that the behavior of water molecules shows singularity near the surfaces of clay minerals. This causes extremely low permeability

and cation diffusivity in bentonite. Here, we showed that local properties can be directly combined with macro-scale behavior using HA procedures. We will continue to evaluate the adsorption-diffusion characteristics of bentonite.

Reference

- Atkins, P.W., 1998, *Physical Chemistry*, 6-th ed., Oxford Univ. Pr.
- Auriault, J.-L., and J. Lewandowska, 1997, "Effective diffusion coefficient: From homogenization to experiment", *Trans. Porous Media*, **27**, 205-223.
- Bear, J. and A. Verruijt, 1987, *Modeling Groundwater Flow and Pollution*, D. Reidel Pub.
- Bowen, R.M., 1976, "Theory of mixture", in *Continuum Physics*, vol. III, ed. by A.C. Eringen, Academic Press, 1-127.
- Fu, M.H., Z.Z. Zhang and P.F. Low, 1990, "Changes in the properties of a montmorillonite-water system during the adsorption and desorption of water hysteresis", *Clays and Clay Minerals*, **38**, 485-492.
- Hornung, U., ed., 1997, *Homogenization and Porous Media*, Springer-Verlag.
- Ichikawa, Y., K. Kawamura, M. Nakano, K. Kitayama and H. Kawamura, 1999, "Unified molecular dynamics and homogenization analysis for bentonite behavior: current results and the future possibility", *Engineering Geology*, **54**, 21-31.
- Japan Nuclear Cycle Development Institute (JNC), 1999, *Second Progress Report on Research and Development for Geological Disposal of High-level Waste in Japan*.
- Kawamura, K., Y. Ichikawa, M. Nakano, K. Kitayama and H. Kawamura, 1997, "New approach for predicting the long term behavior of bentonite: the unified method of molecular simulation and homogenization analysis", *Proc. Sci. Basis for Nuclear Waste Management XXI*, Davos, Swizerland, Material Research Society, Warrendale PA, 359-366.
- Kawamura, K. and Y. Ichikawa, 2001, "Physical properties and chemistry of water and clay minerals", *Bull. Earthquake Research Institute, Univ. Tokyo*, **76** (3), to be appeared.
- Klitzsche, C.S., K. Weistroffer and E.M. Elshasly, 1976, "Grundwasser der Zentralsahara: Fossile Vorräte", *Geol. Rundschau*, **65**, 264.
- Kumagai, N., K. Kawamura and T. Yokokawa, 1994, "An interatomic potential model for H₂O: applications to water and ice polymorphs", *Mol. Simul.*, **12** (3-6), 177-186.
- Langmuir, I., 1918, "The sorption of gases on plane surfaces of glass, mica and platinum", *J. Amer. Chem. Soc.*, **40**, 1361-1403.
- Pusch, R., 1994, *Waste Disposal in Rock*, Elsevier.
- Rowe, R., R.M. Quigley and J. Booker, 1995, *Clayey Barrier Systems for Waste Disposal Facilities*, E & FN Spon.
- Salles, J., J.-F. Thovert, R. Delannay, L. Prevors, J.-L. Auriault and P.M. Adler, 1993, "Taylor dispersion in porous media. Determination of the dispersion tensor", *Phys. Fluids*, **A5** (10), 2348-2376.
- Sanchez-Palencia, E., and A. Zaoui, 1980, *Homogenization Techniques for Composite Media*, Springer-Verlag, Paris.
- Truesdell, C., and R.A. Toupin, 1960, "The classical field theory of mechanics", in *Handbuch der Physik*, ed. by S. Flügge, Springer-Verlag, Berlin.

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