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Electro-osmosis in kaolinite with pH-dependent surface charge modelling by homogenization

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ABSTRACT

A new three-scale model to describe the coupling between pH-dependent flows and transient ion transport, including adsorption phenomena in kaolinite clays, is proposed. The kaolinite is characterized by three separate nano/micro and macroscopic length scales. The pore (micro)-scale is characterized by micro-pores saturated by an aqueous solution containing four monovalent ions and charged solid particles surrounded by thin electrical double layers. The movement of the ions is governed by the Nernst-Planck equations, and the influence of the double layers upon the flow is dictated by the Helmholtz-Smoluchowski slip boundary condition on the tangential velocity. In addition, an adsorption interface condition for the Na^+ transport is postulated to capture its retention in the electrical double layer. The two-scale nano/micro model including salt adsorption and slip boundary condition is homogenized to the Darcy scale and leads to the derivation of macroscopic governing equations. One of the notable features of the three-scale model is the reconstruction of the constitutive law of effective partition coefficient that governs the sodium adsorption in the double layer. To illustrate the feasibility of the three-scale model in simulating soil decontamination by electrokinetics, the macroscopic model is discretized by the finite volume method and the desalination of a kaolinite sample by electrokinetics is simulated.

Key words: electrical double layer, electro-osmosis, homogenization, kaolinite, Nernst-Planck, Poisson-Boltzmann.

INTRODUCTION

The quality of groundwater in clayey soils is strongly influenced by the electrochemistry, which is dictated by the electrochemical interactions that occur between the pore fluid and the minerals. Hydrogeochemical processes, including dissolution, precipitation, ion-exchange, hydrolysis, electroosmosis, electromigration, sorption and desorption, control the variation in chemical composition of groundwater (Mitchell 1993,

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Sposito 1989). Whence, accurate descriptions of such phenomena are of utmost importance when predicting the movement of ionic contaminant plumes, such as heavy metals, coming from improper disposal of sludges and waste water. In addition, the development of comprehensive computational models to study the effectiveness of removal procedures in environmental remediation and clean-up scenarios becomes a crucial issue (Alshawabkeh and Acar 1996, Narasimhan and Sri Ranjan 2000).

The demand for innovative clean-up methods has motivated the development of substantial attempts to use enhanced technologies instead of classical decontamination techniques such as soil flushing, chemical treatment and bioremediation. Among the innovative technologies, electrokinetic remediation became one of the most emerging clean-up procedures successfully reported and cost-effective for remediation of low-permeable soils (Acar et al. 1995, Virkutyte et al. 2002). The effectiveness of this method, particularly its low operation cost, degree of control over the movement of the contaminants, and potential applicability to a wide range of contaminant types, has been the subject of a huge amount of literature (Virkutyte et al. 2002). In recent years, a number of laboratory-scale and field-scale studies have shown the technical feasibility of electrokinetic processes in removing various contaminants from fine-grained soils. The remediation process involves passing a low-level DC electrical current/electrical field between electrode pairs embedded in the polluted soil to induce the movement of electrolyte solution and the transport of soluble contaminants toward the electrodes (Alshawabkeh and Acar 1996).

During the electrokinetic remediation process, the applied electric field consists of the main driving force for phase movement and leads to the well-known electroosmotically induced flow (Mitchell 1993). Electroosmostic phenomenon creates strong electrochemical interactions between the minerals and the aqueous solution, and gives rise to many other macroscopically observed electrochemical processes (Mitchell 1993).

Within the issue of electro-chemo-hydro-mechanical models for colloidal systems, a significant amount of research has been undertaken and a wide range of theories have been developed (Guimarães et al. 2007, Loret et al. 2002). Consequently, different schools of thought have appeared giving rise to purely macroscopic phenomenological approaches (Acar et al. 1995, Narasimhan and Sri Ranjan 2000), models based on Thermodynamics of Irreversible Processes and Onsagers reciprocity relations (Lai et al. 1991) and multiscale methods (Lemaire et al. 2007, Moyne and Murad 2006a). In particular, in order to a better understanding of the correlation between the complex electrical double layer theory at the nanoscale (Hunter 1994) and the macroscopic response of the clay, it becomes essential to develop multiscale approaches (Lemaire et al. 2007, Moyne and Murad 2006a). Such framework has shown a capability of capturing and coarsening the coexistence of several strong couplings of different physicochemical and electrochemical nature occurring at disparate space and time scales (Lima et al. 2008, Moyne and Murad 2006a). Within the framework of two-scale models, phenomena such as electro-osmosis and electromigration naturally appear in the homogenized forms of the convection-diffusion equations and Darcy's law (Moyne and Murad 2006a). This approach has been extended to clay soils composed of two levels of porosity (nano and micro pores) and led to the appearance of three-scale models of dual porosity type (Murad and Moyne 2008).

The aforementioned models were developed for electrolyte solutions composed of two fully dissociated monovalent ions Na^+ and Cl^- and constant $pH = 7$. Consequently, chemical protonation/deprotonation reactions, which occur between the H^+ ions and surface charge groups at the surface of the charged particles, were neglected. The extension of the multiscale procedure to incorporate the pH dependent protonation/deprotonation chemical reactions, giving rise to a nonlinear behavior of the surface charge density, remains an open issue (Dangla et al. 2004). First attempts at incorporating pH effects within the framework of homogenization were pursued in (Lima et al. 2008) for steady flow and ion transport neglecting transient adsorption effects. Thus, the influence of the pH on the magnitude of the partition and retardation coefficients was not discussed. The backbone of the research developed herein is the generalization of the above-mentioned models to incorporate the dependence of transient adsorption on the pH. To accomplish this task, we adopt the formal homogenization procedure of periodic structures based on asymptotic developments (Auriault 1991, Sanchez-Palencia 1980). This approach leads to the derivation of macroscopic governing equations with effective parameters, such as partition coefficient and electro-osmotic permeability, ruled by the electrochemistry that occurs at micro and nanoscale (Fig. 1).

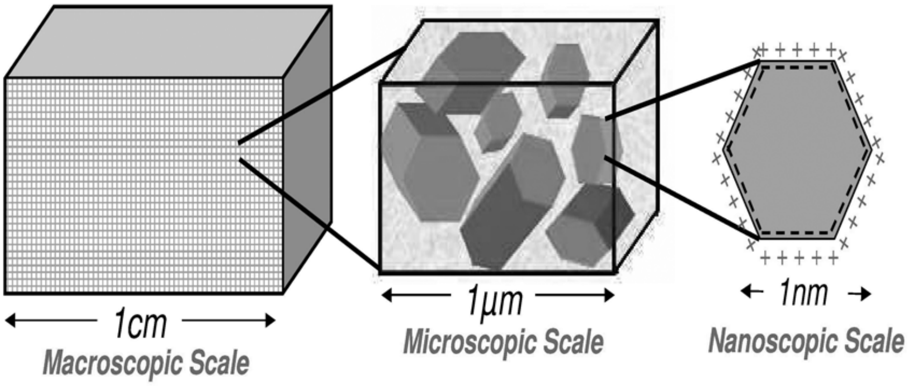


Fig. 1 – Sketch of the three natural length scales in kaolinite (Mitchell 1993).

The three-scale model is discretized by the finite volume method (Patankar 1980) and applied to numerically simulate a transient electro-osmotic experiment of desalination of a kaolinite sample. Boundary conditions of Danckwerts' type are enforced at the anode for the sodium transport governed by the Nernst-Planck equation.

NANOSCALE MODELLING FOR ADSORPTION

We begin by modelling the electro-chemistry of the kaolinite particles at the nanoscale. Consider a two-phase system composed of rigid solid particles that bear an interface charge excess. The solid matrix is filled by a continuum dielectric aqueous dilute solution containing four monovalent electrolytes (Na^+, H^+, Cl^-, OH^-). We adopt the thin electrical double layer (EDL) assumption wherein the Debye's length L_D, whose magnitude is of the same order of the effective thickness of the diffuse layer, is assumed small compared to the characteristic length scale of the micro-pores (Fig. 2(a)). Thus, under this assumption, adjacent double layers do not overlap and, consequently, variations in the electric potential normal to the particle are much more pronounced than in the tangential one. Consequently, under local equilibrium conditions, the electric potential is governed by the Poisson-Boltzmann equation posed in an one-dimensional domain (Hunter 1994). In addition to the ionic concentrations in the electrical double layer, we incorporate adsorption/desorption phenomena owing to protonation/deprotonation reactions involving the H^+ ions at the surface of the particles.

ELECTRICAL DOUBLE LAYER

Let $\{F, R, T\}$ be the set composed of Faraday constant, universal ideal gas constant and absolute temperature, and let φ be the electric potential of the EDL along with C_i and C_{ib}, i =(Na^+, H^+, Cl^-, OH^-), the molar concentration of the ionic species in the EDL and in the bulk fluid, respectively. Denoting $\overline{\varphi} = F\varphi/RT$ the corresponding dimensionless electric potential, the ionic concentrations in the EDL and in the bulk fluid are related by the Boltzmann distribution

$$C_{i^\pm} = C_{ib} \exp\left(\mp\overline{\varphi}\right) \qquad i = (Na^+, H^+, Cl^-, OH^-)\,. \tag{1}$$

Denote $\Omega_*^l = (0, L_D)$ the one-dimensional nanoscopic subdomain in the normal direction to the clay surface occupied by the electrolyte solution with $L_D := \left(\widetilde{\epsilon}_0\widetilde{\epsilon}_r RT/2F^2C_b\right)^{1/2}$ designating the Debye's length (Hunter 1994), $\widetilde{\epsilon}_0$ the permittivity of the free space, $\widetilde{\epsilon}_r$ the dielectric constant of the solvent, and C_b the total concentration of cations (or anions) in the bulk fluid. The electroneutrality condition imposes the constraint

$$C_b = C_{Nab^+} + C_{Hb^+} = C_{Clb^-} + C_{OHb^-} \tag{2}$$

with C_{Hb^+} and C_{OHb^-} ruled by the ionic product of water

$$K_W := C_{Hb^+}C_{OHb^-} = 10^{-8}\left(mol/m^3\right)^2\,. \tag{3}$$

In the usual fashion, let $E = -d\varphi/dz$ be the component of the electric field orthogonal to the surface with z the normal coordinate (Fig. 2(a)), and $q := F\,(C_{Na^+} + C_{H^+} - C_{Cl^-} - C_{OH^-})$ the net charge density. Using the Boltzmann distribution (1), the one-dimensional Poisson-Boltzmann problem reads as

$$\frac{d^2\varphi}{dz^2} = -\frac{q}{\widetilde{\epsilon}_0\widetilde{\epsilon}_r} = \frac{2FC_b}{\widetilde{\epsilon}_0\widetilde{\epsilon}_r}\sinh\overline{\varphi} \qquad \text{in } \Omega^l := (0, \ell_*) \tag{4}$$

where $z = \ell_*$ refers to a point further away from the interface ($\ell_* > L_D$). The above equation is supplemented by boundary conditions at particle wall $z = 0$ and at the distance $z = \ell_*$. For non-overlapping adjacent EDLs, the electric field at $z = \ell_*$ vanishes, whereas at the particle surface the electrical field balances the surface charge density σ

$$\frac{d\varphi}{dz} = 0 \text{ at } z = \ell_* \qquad \text{and} \qquad \frac{d\varphi}{dz} = -\frac{\sigma}{\widetilde{\epsilon}_0\widetilde{\epsilon}_r} \text{ at } z = 0\,. \tag{5}$$

The unidimensional Poisson-Boltzmann problem (4) together with boundary conditions (5) govern the local behavior of electric potential at the nanoscale around the kaolinite particle. Under the thin double layer assumptions, an analytical relation between φ and the zeta potential $\zeta := \varphi(z = 0)$ can be obtained (Lima et al. 2008)

$$\varphi = \frac{4RT}{F}\operatorname{arctanh}\left[\tanh\left(\frac{F\zeta}{4RT}\right)\exp\left(-\frac{z}{L_D}\right)\right]. \tag{6}$$

Further combining (5(b)) and (6), and using the definition of L_D, we deduce the following relation between σ and ζ

$$\sigma = \frac{2\widetilde{\epsilon}_0\widetilde{\epsilon}_r RT}{FL_D}\sinh\left(\frac{F\zeta}{2RT}\right) = \sqrt{8\widetilde{\epsilon}_0\widetilde{\epsilon}_r RTC_b}\,\sinh\left(\frac{F\zeta}{2RT}\right). \tag{7}$$

The surface charge density of the particles attracts the counter-ions to the vicinity of the mineral, giving rise to the adsorption/desorption capacity of the EDL Γ_i i =(Na^+, H^+, Cl^-, OH^-). The definition of Γ_i reads as

$$\Gamma_{i^\pm} := \int_{z=0}^{z=L_D} \left(C_{i^\pm} - C_{i_b} \right) dz \,. \tag{8}$$

To derive the analytical representation of Γ_i, we introduce the dimensionless coordinate $\overline{z} = z/L_D$ normal to the surface, multiply the Poisson-Boltzmann equation (4) by $2d\overline{\varphi}/d\overline{z}$ and use the chain rule. After integrating from an arbitrary $\overline{z}$ inside the EDL to the point $\overline{\ell}_* = \ell_*/L_D$ in the bulk solution, using the thin double layer assumption, we obtain

$$\left(\frac{d\overline{\varphi}}{d\overline{z}} \right)^2 = 2 \left(\cosh \overline{\varphi} - 1 \right) \,. \tag{9}$$

Using the relation $\sinh(\overline{\varphi}/2) = \left[\left(\cosh \overline{\varphi} - 1 \right)/2 \right]^{1/2}$, this equality can be rephrased as

$$-d\overline{z} = \frac{d\overline{\varphi}}{2\sinh\left(\dfrac{\overline{\varphi}}{2}\right)} = \frac{d\overline{\varphi}}{\exp\left(\dfrac{\overline{\varphi}}{2}\right) - \exp\left(\dfrac{-\overline{\varphi}}{2}\right)}$$

The nanoscopic representation of Γ_i can be obtained using (1) in (8) along with the above change of variable. This yields

$$\Gamma_{i^\pm} = -C_{i_b} L_D \int_{\zeta}^{\varphi=0} \left[\frac{\exp(\mp\overline{\varphi}) - 1}{\exp\left(\frac{\overline{\varphi}}{2}\right) - \exp\left(\frac{-\overline{\varphi}}{2}\right)} d\overline{\varphi} \right] = 2C_{i_b} L_D \left[\exp\left(\mp \frac{F\zeta}{2RT} \right) - 1 \right] \tag{10}$$

As the surface charge and the ζ-potential vary strongly with the pH of the electrolyte solution, the closure of the system is tied-up to the construction of this dependence that can be accomplished by invoking the kinetics of the protonation/deprotonation reactions presented next (Chorover and Sposito 1995, Ganor et al. 2003, Huertas et al. 1997).

PROTONATION/DEPROTONATION CHEMICAL REACTION

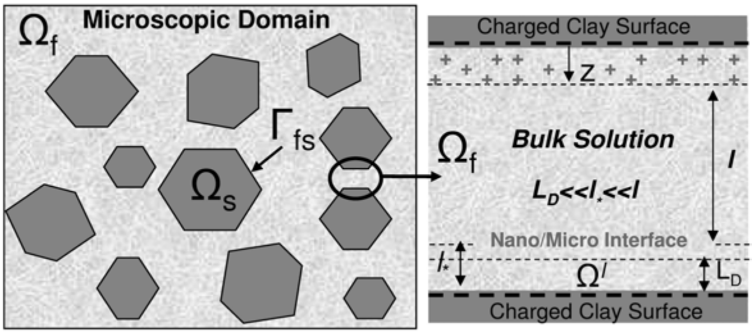
In addition to the ion adsorption in the EDL, protonation/deprotonation reactions take place at particle edges. Considering hexagonal form of the kaolinite particles (Mitchell 1993), we assume that the charge due to isomorphous substitutions on the basal hydroxyl and siloxane planes are negligible compared to the one produced by broken bonds on the lateral edges (Fig. 2(b)) (Brady et al. 1996).

1-pK model

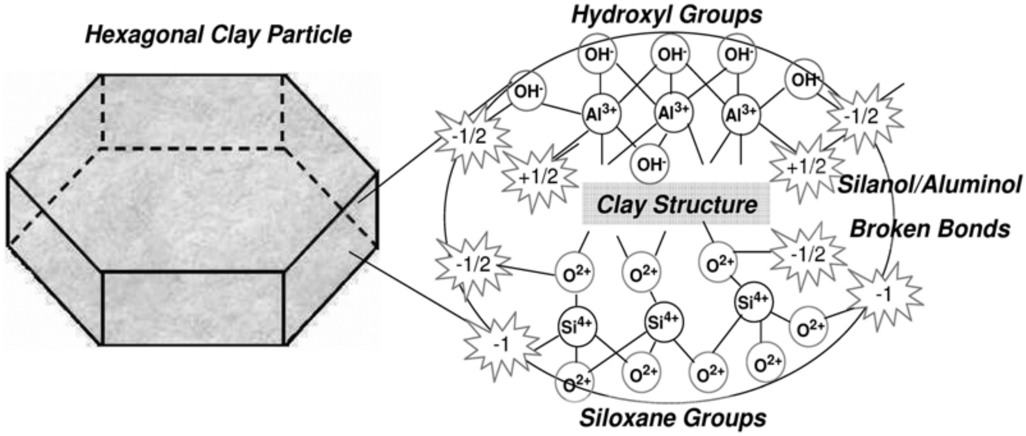
We adopt a model based on a single protonation/deprotonation chemical reaction. Denoting M a metallic ion lying in the tetrahedral (Si^{4+}) or octahedral (Al^{3+}) layers, and K the equilibrium constant associated with the chemical reaction, under the assumption of local equilibrium, the protonation/deprotonation reaction can be represented in the form

$$(> M - OH)^{-\frac{1}{2}} + H^+ \rightleftharpoons (> M - OH_2)^{+\frac{1}{2}}$$

$$K := \frac{\left\{ (> M - OH_2)^{+\frac{1}{2}} \right\}}{\left\{ (> M - OH)^{-\frac{1}{2}} \right\} C_{H_0^+}} \tag{11}$$



(a) Description of the Electrical Double Layer (EDL).



(b) Kaolinite particle geometry with structure composed of siloxane/hydroxyl planes and broken bond edges.

Fig. 2 – EDL and mineralogic structures of kaolinite.

where $\{j\} = \gamma_j/\Gamma_{MAX}$ is the dimensionless surface concentration of the **j** species, γ_j the surface density of the reagent/product ($j = M - OH, M - OH_2$),

$$\Gamma_{MAX} := \gamma_{\left\{(>M-OH_2)^{+\frac{1}{2}}\right\}} + \gamma_{\left\{(>M-OH)^{-\frac{1}{2}}\right\}}$$

the maximum surface density (mol/m^2) and $C_{H_0^+} = C_{Hb^+} \exp(-F\zeta/RT)$ the H^+ concentration at the kaolinite surface (mol/l). From the above definition, the excess in surface charge due to the protonic adsorption γ_{H^+} is defined as

$$\sigma := Fz\gamma_{H^+} := Fz\left(\gamma_{\left\{(>M-OH_2)^{+\frac{1}{2}}\right\}} - \gamma_{\left\{(>M-OH)^{-\frac{1}{2}}\right\}}\right)X \tag{12}$$

where $z = 1/2$ is the valence. To complete the characterization of σ, one needs to postulate a constitutive law for γ_{H^+} that can be obtained by rewriting (11) in the form

$$\gamma_{\left\{(>M-OH_2)^{+\frac{1}{2}}\right\}} = K\gamma_{\left\{(>M-OH)^{-\frac{1}{2}}\right\}}C_{H_0^+}$$

which, together with the definition of the maximum surface density Γ_{MAX}, gives

$$\gamma_{\left\{(>M-OH)^{-\frac{1}{2}}\right\}} = \frac{\Gamma_{MAX}}{1 + KC_{H_0^+}} \qquad \gamma_{\left\{(>M-OH_2)^{+\frac{1}{2}}\right\}} = \frac{\Gamma_{MAX}KC_{H_0^+}}{1 + KC_{H_0^+}} \tag{13}$$

Using (13) in (12), we deduce

$$\gamma_{H^+} := \left(\gamma_{\left\{(>M-OH_2)^{+\frac{1}{2}}\right\}} - \gamma_{\left\{(>M-OH)^{-\frac{1}{2}}\right\}}\right) = \Gamma_{MAX}\left(\frac{KC_{H_0^+}-1}{KC_{H_0^+}+1}\right) \tag{14}$$

and

$$\sigma := \frac{F\gamma_{H^+}}{2} = \frac{F\Gamma_{MAX}}{2}\left(\frac{KC_{H_0^+}-1}{KC_{H_0^+}+1}\right). \tag{15}$$

The above results provide the constitutive laws for the pair $(\sigma,\ \gamma_{H^+})$. Experimental data for the constants K and Γ_{MAX} can be obtained by performing an optimization procedure between our model and the titration experiments reported by Huertas (Huertas et al. 1997). This yields $K = 10^{5.5}\ l/mol$ and $\Gamma_{MAX} = 3.0$ sites/nm^2 (Lima et al. 2008). The model for the particle-fluid interface is now established: given the values $(C_{ib},\ L_D)$ $(i = Na^+,\ H^+,\ Cl^-,\ OH^-)$, by collecting the results (1), (7) and (15), our nanoscopic model consists of solving the following set of nonlinear algebraic equations for the unknowns $(C_{H_0^+}, \sigma, \zeta)$

$$\begin{cases} C_{H_0^+} = C_{Hb^+}\exp\left(-\dfrac{F\zeta}{RT}\right) \\ \sigma = (8\widetilde{\epsilon}_0\widetilde{\epsilon}_r RTC_b)^{1/2}\sinh\left(\dfrac{F\zeta}{2RT}\right) \\ \sigma = \dfrac{F\Gamma_{MAX}}{2}\left(\dfrac{KC_{H_0^+}-1}{KC_{H_0^+}+1}\right) \end{cases} \tag{16}$$

After computing the constitutive dependence of the ζ-potential, we can make use of (10) to quantify the EDL exchange capacity Γ_i.

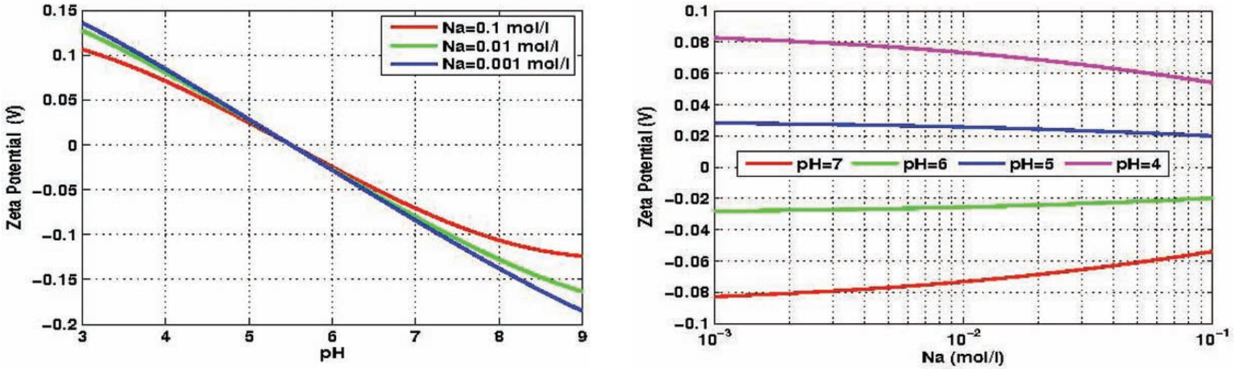
The numerical constitutive relations $\zeta = \zeta(C_{Nab^+}, C_{Hb^+})$ and $\Gamma_{Na} = \Gamma_{Na}(C_{Nab^+}, C_{Hb^+})$ are depicted in Figure 3. We observe a stronger dependence of the ζ-potential on the pH than on the Na^+. In the basic regime ($pH > 5.5$), the ζ-potential becomes negative and, consequently, the Na^+ immobilization in the EDL increases and vice-versa in the acid regime (Fig. 3). Regarding the constitutive response of ζ and Γ_{Na^+} with salinity, we may note that, in the acid regime ($pH < 5.5$), an increase in salinity leads to an increase in the positivity of the ζ-potential, which implies in the desorption of the Na^+.

MICROSCOPIC MODELLING

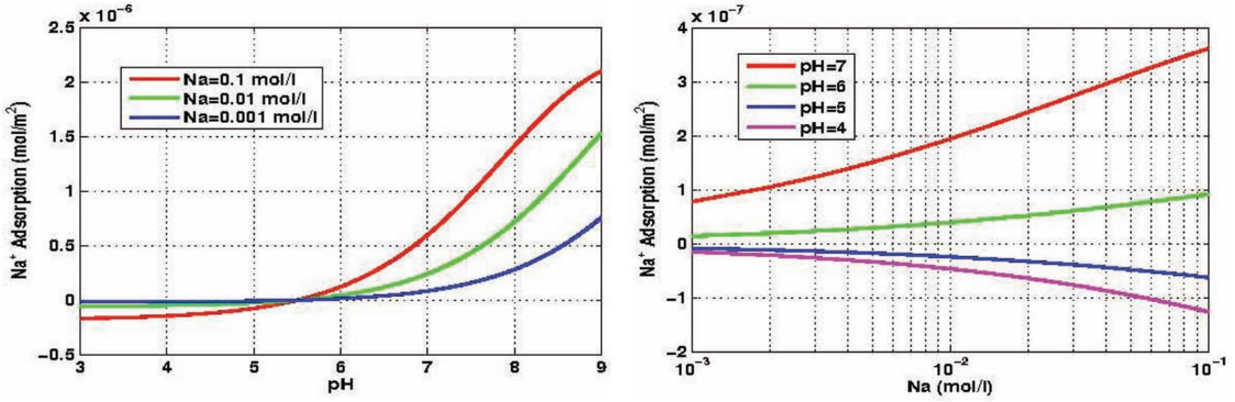
At the microscale, the clay is envisioned as a two-phase system composed of kaolinite particles and micro-pores filled by an aqueous solution. The characteristic length of the macro-pores l of $O(10^{-6}m)$ is much greater than the nanoscopic thickness of the EDL. Whence, the nanoscopic descriptions of the ζ-potential and EDL adsorption are incorporated in the microscopic model through an effective boundary condition.

Microscopic Governing Equations

Following the usual framework of multiscale models, we begin by establishing the governing equation at the microscale. Let $\Omega = \Omega_s \cup \Omega_f \subset \Re^3$ be the microscopic domain occupied by the biphasic porous media composed of solid particles and micro-pores, and Γ_{fs} the boundary between the solid and fluid subdomains (Fig. 2(a)). The solid domain Ω_s is formed by kaolinite particles carrying the surface charge density. The



(a) Zeta Potential as a function of pH. (b) Zeta Potential as a function of Na^+.



(c) Na^+ Adsorption as a function of pH. (d) Na^+ Adsorption as a function of Na^+.

Fig. 3 – Dependence of the zeta potential and Na^+ EDL adsorption on pH and C_{Nab^+}.

subdomain Ω_f is occupied by the bulk solution containing four ionic monovalent solutes (Na^+, H^+, Cl^-, OH^-). We assume that H^+ and OH^- ions reach the equilibrium in a much faster time scale compared to the one associated with the movement of Na^+ and Cl^-. Under this assumption, the pH of the bulk solution is constant, but its magnitude plays a crucial role in the hydrodynamics and transport of Na^+ and Cl^- (Lima et al. 2008). In our subsequent analysis, we consider the aqueous solution movement and Na^+/Cl^- transport governed by the classical theory of viscous fluids and transient Nernst-Planck equations, respectively (Samson et al. 1999).

Hydrodynamics

Assuming the bulk fluid as an aqueous Newtonian incompressible solution, neglecting gravity and convection/inertial effects, the hydrodynamics is governed by the classical Stokes problem

$$\begin{aligned} &\nabla \cdot \mathbf{v} = 0 \\ &\mu_f \Delta \mathbf{v} - \nabla p = 0 \qquad \text{in } \Omega_f \end{aligned} \tag{17}$$

where $\mathbf{v}$ is the fluid velocity, p the pressure and μ_f the water viscosity.

Ion Transport

In addition to the advection induced by the velocity $\mathbf{v}$, ion diffusion is due to the sum of Fickian and electromigration components that govern the spreading of the ionic species under concentrations and electric potential gradients, respectively (Sherwood 1994). Denoting t the characteristic time scale of the transport, the Na^+ and Cl^- movements are governed by the Nernst-Planck equation (Samson et al. 1999)

$$\begin{aligned}
&\frac{\partial C_{Nab^+}}{\partial t} + \nabla \cdot (C_{Nab^+}\mathbf{v}) - \nabla \cdot \left[D_{Na^+} \left(\nabla C_{Nab^+} + C_{Nab^+} \nabla \overline{\phi} \right) \right] = 0 \\
&\frac{\partial C_{Clb^-}}{\partial t} + \nabla \cdot (C_{Clb^-}\mathbf{v}) - \nabla \cdot \left[D_{Cl^-} \left(\nabla C_{Clb^-} - C_{Clb^-} \nabla \overline{\phi} \right) \right] = 0 \qquad \text{in } \Omega_f
\end{aligned} \tag{18}$$

where D_i refers to the binary water-ion diffusion coefficients ($i = Na^+, Cl^-$) and $\overline{\phi} := F\phi/RT$ the dimensionless microscopic electrical potential.

To derive the equation for the conservation of charge, we begin by defining the electric current $\mathbf{I_f}$

$$\begin{aligned}
&\mathbf{I_f} := F\left(\mathbf{J_{Na^+}} - \mathbf{J_{Cl^-}}\right) \qquad \text{where} \\
&\mathbf{J_i} := C_{ib}\mathbf{v} - D_i\left(\nabla C_{ib} \pm C_{ib}\nabla\overline{\phi}\right) \qquad (i = Na^+, Cl^-)
\end{aligned}$$

denotes the total convective/diffusive ionic flux of each solute. By subtracting the Nernst-Planck relations (18) for the Cl^- from the Na^+, using the above definition together with the electroneutrality condition (2) and the ionic product of water (3) by recalling our time scale assumption, where C_{Hb^+} and C_{OHb^-} are assumed constant, we obtain conservation of charge

$$\nabla \cdot \left(A \nabla C_{Nab^+} + B \nabla \overline{\phi} \right) = 0 \tag{19}$$

with the new coefficients given by

$$\begin{aligned}
&A := F\left(D_{Na^+} - D_{Cl^-}\right) \\
&B := F\left[\left(D_{Na^+} + D_{Cl^-}\right) C_{Nab^+} + D_{Cl^-} \left(1 - \frac{K_W}{C_{Hb^+}^2} \right) C_{Hb^+} \right]
\end{aligned} \tag{20}$$

Boundary conditions

We begin by establishing the proper velocity interface condition for the Stokes problem (17). Owing to the presence of the thin electrical double layer surrounding each kaolinite particle, we postulate the so-called Smoluchowsky slip boundary condition (Murad and Moyne 2008) wherein the tangential velocity exhibits a discontinuity at the interface. We, then, have

$$\begin{aligned}
&\mathbf{v} \cdot \boldsymbol{\tau} = \frac{\widetilde{\epsilon}_0 \widetilde{\epsilon}_r \zeta}{\mu_f} \nabla \phi \cdot \boldsymbol{\tau} \\
&\mathbf{v} \cdot \mathbf{n} = 0 \qquad \text{on } \Gamma_{fs}
\end{aligned}$$

It remains to establish the interface conditions for the Nernst-Planck equations. To this end, we invoke the conservation of mass at the interface, which states that the time derivative of the EDL adsorption quantities $\Gamma_i(i = Na^+)$ balances the diffusive flux normal to the particle surface (Auriault and Lewandowska 1996). Recalling the constitutive law for the EDL adsorption reconstructed from the nanoscopic modelling $\Gamma_{Na^+} = \Gamma_{Na^+}(C_{Nab^+}, C_{Hb^+})$ and the assumption of constant pH, using the chain rule, the boundary conditions are given by

$$\begin{aligned} &- D_{Na^+}\left(\nabla C_{Nab^+} + C_{Nab^+}\nabla\overline{\phi}\right)\cdot\mathbf{n} = K_d\frac{\partial C_{Nab^+}}{\partial t} \\ &\left(A\nabla C_{Nab^+} + B\nabla\overline{\phi}\right)\cdot\mathbf{n} = 0 \qquad\qquad \text{on } \Gamma_{fs} \end{aligned}$$

where $K_d := \partial\Gamma_{Na^+}/\partial C_{Nab^+}$ is the partition coefficient.

SUMMARY OF THE TWO SCALE MODEL

The two-scale nanoscopic/microscopic model consists in: given the constants $\{\mu_f, K_W, D_{Na^+}, D_{Cl^-}$, F, R, T, A, $C_{Hb^+}\}$, the electric conductivity B depending on C_{Nab^+} and C_{Hb^+} find, the microscopic fields $\{\mathbf{v}, p, C_{Nab^+}, \phi\}$ satisfying

$$\begin{cases} \nabla\cdot\mathbf{v} = 0 \\ \mu_f\triangle\mathbf{v} - \nabla p = 0 \\ \dfrac{\partial C_{Nab^+}}{\partial t} + \nabla\cdot(C_{Nab^+}\mathbf{v}) = \nabla\cdot\left[D_{Na^+}\left(\nabla C_{Nab^+} + C_{Nab^+}\nabla\overline{\phi}\right)\right] \\ \nabla\cdot\left(A\nabla C_{Nab^+} + B\nabla\overline{\phi}\right) = 0 \end{cases} \quad \text{in } \Omega_f \tag{21}$$

supplemented by boundary conditions

$$\begin{cases} \mathbf{v}\cdot\boldsymbol{\tau} = \dfrac{\widetilde{\epsilon}_0\widetilde{\epsilon}_r\zeta}{\mu_f}\nabla\phi\cdot\boldsymbol{\tau} \\ \mathbf{v}\cdot\mathbf{n} = 0 \\ -D_{Na^+}\left(\nabla C_{Nab^+} + C_{Nab^+}\nabla\overline{\phi}\right)\cdot\mathbf{n} = K_d\dfrac{\partial C_{Nab^+}}{\partial t} \\ \left(A\nabla C_{Nab^+} + B\nabla\overline{\phi}\right)\cdot\mathbf{n} = 0 \end{cases} \quad \text{on } \Gamma_{fs} \tag{22}$$

As we shall observe next, by invoking the constitutive responses of the zeta potential $\zeta = \zeta(C_{Nab^+}, C_{Hb^+})$ and EDL adsorption coefficient $\Gamma_{Na^+} = \Gamma_{Na^+}(C_{Nab^+}, C_{Hb^+})$ reconstructed from the nanoscopic modelling in Figure 3, we can build-up the response functions for the electroosmotic permeability $K_E = K_E(C_{Nab^+}, C_{Hb^+})$ and partition coefficient $K_d := \partial\Gamma_{Na^+}/\partial C_{Nab^+} = K_d(C_{Nab^+}, C_{Hb^+})$.

HOMOGENIZATION

In this section, we apply the asymptotic homogenization theory (Sanchez-Palencia 1980) to upscale the microscopic model to the macroscale. The kaolinite is characterized by a periodic structure with two disparate length scales: the microscopic scale l of the order of the size of the micropores, and the macroscopic length scale L of the overall dimension of the medium. Within the framework of homogenization, we introduce the perturbation parameter $\varepsilon = l/L$ whose magnitude, under the assumption of scale separation, is $\varepsilon \ll 1$.

To capture the correct physics in the process of up-scaling, the coefficients of the microscopic model must be properly scaled in powers of ε. This is accomplished by estimating the dimensionless quantities in the local description. Following the classical homogenization analysis of the Stokes problem, the fluid viscosity is scaled by ε^2 (Auriault 1991). Further, we assume convective and diffusive effects of the same order of magnitude, so that the Peclet number Pe is of $O(1)$. Denoting t_{ref} a reference time for the EDL adsorption, we follow Auriault (Auriault and Lewandowska 1996) and consider the case wherein the Dankholer number $Da = K_d L / D_{Na^+} t_{ref}$, which measures the ratio between adsorption and diffusion at the interface, is of $O(\varepsilon)$.

MATCHED ASYMPTOTIC EXPANSION

To upscale the microscopic model to the macroscale, we adopt the formal homogenization procedure based on perturbation expansions (Auriault 1991, Sanchez-Palencia 1980). Within this framework, each property is considered dependent on both global and local length scales in the form $f = f(\mathbf{x}, \mathbf{y})$, where $\mathbf{x}$ and $\mathbf{y}$ denote the macroscopic and microscopic coordinates, respectively. Up to a translation, $\mathbf{x}$ and $\mathbf{y}$ are related by $\mathbf{y} = \mathbf{x}/\varepsilon$. By the chain rule, the differential operator is replaced by $\nabla = \nabla_x + \varepsilon^{-1}\nabla_y$. The usual procedure to obtain the homogenized problem consists in postulating asymptotic expansions for the unknowns

$$f^{\varepsilon}(\mathbf{x}, \mathbf{y}) = \sum_{k=0}^{\infty} \varepsilon^k f^k(\mathbf{x}, \mathbf{y})$$

with the functions $f^i = f^i(\mathbf{x}, \mathbf{y})$ $(i = 0, 1, 2...)$ $\mathbf{y}$-periodic. Inserting the ansatz into the microscopic governing equations and collecting the powers of ε, we obtain successive equations at different orders

$$\nabla_y \cdot \left[D_{Na^+} \left(\nabla_y C^0_{Nab^+} + C^0_{Nab^+} \nabla_y \overline{\phi}^0 \right) \right] = 0 \tag{23}$$

$$\nabla_y \cdot \left(A \nabla_y C^0_{Nab^+} + B^0 \nabla_y \overline{\phi}^0 \right) = 0 \tag{24}$$

$$\nabla_y \cdot \mathbf{v}^0 = 0 \tag{25}$$

$$\nabla_y p^0 = 0 \tag{26}$$

$$\nabla_y \cdot \left(C^0_{Nab^+} \mathbf{v}^0 \right) + \nabla_x \cdot \left[D_{Na^+} \left(\nabla_y C^0_{Nab^+} + C^0_{Nab^+} \nabla_y \overline{\phi}^0 \right) \right] + \nabla_y \cdot \mathbf{J}^{\mathbf{0}}_{\mathbf{Na}^+} = 0 \tag{27}$$

$$\nabla_x \cdot \left(A \nabla_y C^0_{Nab^+} + B^0 \nabla_y \overline{\phi}^0 \right) + \nabla_y \cdot \mathbf{I}^{\mathbf{0}}_{\mathbf{f}} = 0 \tag{28}$$

$$\mathbf{J}^{\mathbf{0}}_{\mathbf{Na}^+} = -D_{Na^+} \left[\left(\nabla_x C^0_{Nab^+} + \nabla_y C^1_{Nab^+} \right) + C^0_{Nab^+} \left(\nabla_x \overline{\phi}^0 + \nabla_y \overline{\phi}^1 \right) + C^1_{Nab^+} \nabla_y \overline{\phi}^0 \right] \tag{29}$$

$$\mathbf{I}^{\mathbf{0}}_{\mathbf{f}} = A \left(\nabla_x C^0_{Nab^+} + \nabla_y C^1_{Nab^+} \right) + B^0 \left(\nabla_x \overline{\phi}^0 + \nabla_y \overline{\phi}^1 \right) + B^1 \nabla_y \overline{\phi}^0 \tag{30}$$

$$\nabla_x \cdot \mathbf{v}^0 + \nabla_y \cdot \mathbf{v}^1 = 0 \tag{31}$$

$$\mu_f \triangle_{yy} \mathbf{v}^0 - \nabla_y p^1 = \nabla_x p^0 \tag{32}$$

$$\begin{aligned} &\frac{\partial C^0_{Nab^+}}{\partial t} + \nabla_x \cdot \left(C^0_{Nab^+} \mathbf{v}^0 \right) + \nabla_y \cdot \left(C^0_{Nab^+} \mathbf{v}^1 + C^1_{Nab^+} \mathbf{v}^0 \right) \\ &\qquad + \nabla_x \cdot \mathbf{J}^{\mathbf{0}}_{\mathbf{Na}^+} + \nabla_y \cdot \mathbf{J}^{\mathbf{1}}_{\mathbf{Na}^+} = 0 \end{aligned} \tag{33}$$

$$\nabla_x \cdot \mathbf{I}^{\mathbf{0}}_{\mathbf{f}} + \nabla_y \cdot \mathbf{I}^{\mathbf{1}}_{\mathbf{f}} = 0 \tag{34}$$

whereas the successive orders of the interface conditions read as

$$\left[D_{Na^+}\left(\nabla_y C^0_{Nab^+} + C^0_{Nab^+}\nabla_y \overline{\phi}^0\right)\right]\cdot \mathbf{n} = 0 \tag{35}$$

$$\left(A\nabla_y C^0_{Nab^+} + B^0\nabla_y \overline{\phi}^0\right)\cdot \mathbf{n} = 0 \tag{36}$$

$$\mathbf{v}^0\cdot\mathbf{n} = 0 \tag{37}$$

$$\mathbf{v}^1\cdot\mathbf{n} = 0 \tag{38}$$

$$\mathbf{v}^0\cdot\boldsymbol{\tau} = \frac{\widetilde{\epsilon}_0\widetilde{\epsilon}_r}{\mu_f}\left[\zeta^0\left(\nabla_x\phi^0 + \nabla_y\phi^1\right) + \zeta^1\nabla_y\phi^0\right]\cdot\boldsymbol{\tau} \tag{39}$$

$$\mathbf{J^0_{Na^+}}\cdot\mathbf{n} = 0 \tag{40}$$

$$\mathbf{I^0_f}\cdot\mathbf{n} = 0 \tag{41}$$

$$\mathbf{J^1_{Na^+}}\cdot\mathbf{n} = K^0_d\frac{\partial C^0_{Nab^+}}{\partial t} \tag{42}$$

$$\mathbf{I^1_f}\cdot\mathbf{n} = 0 \tag{43}$$

Using classical arguments of the formal homogenization procedure (Lima et al. 2008), our set of non-oscillatory variables, depending only on (x, t), is $\{p^0, C^0_{Nab^+}, \overline{\phi}^0, \zeta^0, B^0, V^0_{slip}, K^0_d\}$. In addition, the closure problems for the fluctuations $\{C^1_{Nab^+}, \phi^1\}$ are given by the linear relations

$$\begin{aligned}C^1_{Nab^+}(\mathbf{x},\mathbf{y},t) &= \mathbf{f}(\mathbf{y})\cdot\nabla_x C^0_{Nab^+}(\mathbf{x},t) + \widetilde{C}_{Na^+}(\mathbf{x},t)\\ \overline{\phi}^1(\mathbf{x},\mathbf{y},t) &= \mathbf{f}(\mathbf{y})\cdot\nabla_x\overline{\phi}^0(\mathbf{x},t) + \widetilde{\phi}(\mathbf{x},t)\end{aligned} \tag{44}$$

with the characteristic tortuosity vectorial function $\mathbf{f} = \mathbf{f}(\mathbf{y})$ satisfying the canonical Neumann problem

$$\left\{\begin{array}{lcll}\triangle_{yy}\mathbf{f}(\mathbf{y}) & = & 0 & \text{in } Y\\ \nabla_y\mathbf{f}(\mathbf{y})\,\mathbf{n} & = & -\mathbf{n} & \text{on } \partial Y_{fs}\end{array}\right. . \tag{45}$$

To derive the macroscopic Nernst-Planck equation for the Na^+ transport, we begin by introducing the volume averaging operator over the periodic cell

$$\langle\chi\rangle := \frac{1}{|Y|}\int_{Y_f}\chi\,d\mathbf{y} \qquad\qquad \langle\chi\rangle_{fs} := \frac{1}{|Y|}\int_{\partial\Gamma_{fs}}\chi\,d\mathbf{y}\,.$$

By averaging (33), we obtain

$$\left\langle\frac{\partial C^0_{Nab^+}}{\partial t}\right\rangle + \left\langle\nabla_x\cdot\left(C^0_{Nab^+}\mathbf{v}^0\right)\right\rangle + \left\langle\nabla_y\cdot\left(C^0_{Nab^+}\mathbf{v}^1 + C^1_{Nab^+}\mathbf{v}^0\right)\right\rangle + \left\langle\nabla_x\cdot\mathbf{J^0_{Na^+}} + \nabla_y\cdot\mathbf{J^1_{Na^+}}\right\rangle = 0$$

Recalling that $\{C^0_{Nab^+}, \overline{\phi}^0\}$ are $\mathbf{y}$-independent, defining $\eta := |Y_f|/|Y|$ and $\mathbf{V^0_D} := \langle\mathbf{v^0}\rangle$ the macroscopic porosity and Darcy's velocity, respectively, using Gauss theorem and the interface condition (42) gives

$$\eta\frac{\partial C^0_{Nab^+}}{\partial t} + \nabla_x\cdot\left(C^0_{Nab^+}\mathbf{V^0_D}\right) + \nabla_x\cdot\left\langle\mathbf{J^0_{Na^+}}\right\rangle = -\int_{\partial\Gamma_{fs}}\mathbf{J^1_{Na^+}}\cdot\mathbf{n}\,d\Gamma = -\left\langle K^0_d\right\rangle_{fs}\frac{\partial C^0_{Nab^+}}{\partial t}$$

Using the constitutive law for the flux (29) along with the closure relations in (44), we obtain the macroscopic result

$$\begin{aligned} &R^0 \frac{\partial C^0_{Nab^+}}{\partial t} + \nabla_x \cdot \mathbf{J}^{\mathbf{eff}}_{\mathbf{Na}^+} = 0 \\ &\mathbf{J}^{\mathbf{eff}}_{\mathbf{Na}^+} = C^0_{Nab^+}\mathbf{V}^{\mathbf{0}}_{\mathbf{D}} + \nabla_x \cdot \left[\mathbf{D}^{\mathbf{eff}}_{\mathbf{Na}^+}\left(\nabla_x C^0_{Nab^+} + C^0_{Nab^+}\nabla_x \overline{\phi}^0\right)\right] \end{aligned}$$

with the effective diffusivities and the retardation coefficients defined as

$$\mathbf{D}^{\mathbf{eff}}_{\mathbf{Na}^+} := D_{Na^+}\big\langle \mathbf{I} + \nabla_y \mathbf{f}\,(\mathbf{y})\,\big\rangle \qquad R^0 := \eta + \big\langle K^0_d\big\rangle_{fs}\,.$$

The effective charge conservation equation can be obtained in a straightforward fashion. By averaging (34) and using boundary condition (43), we obtain

$$\nabla_x \cdot \big\langle \mathbf{I}^{\mathbf{0}}_{\mathbf{f}}\big\rangle = 0\,.$$

Denoting $\mathbf{I}^{\mathbf{eff}}_{\mathbf{f}} := \big\langle \mathbf{I}^{\mathbf{0}}_{\mathbf{f}}\big\rangle$ the effective current, by combining (44) for the concentration and potential fluctuations with (30), we obtain the macroscopic constitutive law

$$\mathbf{I}^{\mathbf{eff}}_{\mathbf{f}} = \mathbf{A}^{\mathbf{eff}}\nabla_x C^0_{Nab^+} + \mathbf{B}^{\mathbf{eff}}\nabla_x \overline{\phi}^0$$

with the effective parameters given as

$$\mathbf{A}^{\mathbf{eff}} := A\big\langle \mathbf{I} + \nabla_y \mathbf{f}\,(\mathbf{y})\,\big\rangle \qquad \mathbf{B}^{\mathbf{eff}} := B^0\big\langle \mathbf{I} + \nabla_y \mathbf{f}\,(\mathbf{y})\,\big\rangle\,.$$

To derive the macroscopic form of Darcy's law, we begin by using the closure relation for the electric potential (44) in (39) to obtain for the slip velocity

$$V^0_{slip} = \frac{\widetilde{\epsilon}_0\widetilde{\epsilon}_r\zeta^0}{\mu_f}\big(\mathbf{I} + \nabla_y \mathbf{f}\big)\,\nabla_x\phi^0 \cdot \boldsymbol{\tau}\,.$$

Combining the above result with the mass balance (25) and the momentum equation (32), we obtain the local Stokes problem formulated in terms of the pair ($\mathbf{v}^0$, p^1)

$$\begin{cases} \mu_f \triangle_{yy}\mathbf{v}^0 - \nabla_y p^1 = \nabla_x p^0 & \\ \nabla_y \cdot \mathbf{v}^0 = 0 & \text{in } \; Y_f \\ \mathbf{v}^0 \cdot \mathbf{n} = 0 & \\ \mathbf{v}^0 \cdot \boldsymbol{\tau} = \dfrac{\widetilde{\epsilon}_0\widetilde{\epsilon}_r\zeta^0}{\mu_f}\big(\mathbf{I} + \nabla_y \mathbf{f}\big)\,\nabla_x\phi^0 \cdot \boldsymbol{\tau} & \text{on } \; \partial Y_{fs} \end{cases}$$

To derive Darcy's Law, we proceed in a similar fashion to (Lima et al. 2008). This yields

$$\mathbf{V}^{\mathbf{0}}_{\mathbf{D}} = \langle \mathbf{v}^{\mathbf{0}}\rangle = -\mathbf{K}^{\mathbf{eff}}_{\mathbf{P}}\nabla_x p^0 - \mathbf{K}^{\mathbf{eff}}_{\mathbf{E}}\nabla_x\phi^0 \tag{46}$$

where the effective conductivities are defined as

$$\mathbf{K}^{\mathbf{eff}}_{\mathbf{P}} := \langle \boldsymbol{\kappa}_{\boldsymbol{P}}\rangle \qquad \mathbf{K}^{\mathbf{eff}}_{\mathbf{E}} := -\frac{\widetilde{\epsilon}_0\widetilde{\epsilon}_r\zeta^0}{\mu_f}\big\langle \mathbf{I} + \nabla_y \mathbf{f}\big\rangle \tag{47}$$

with the vectorial component of characteristic function $\boldsymbol{\kappa}_{\boldsymbol{P}}^{\boldsymbol{j}}$, $(j = 1, 2, 3)$ given by

$$\begin{aligned} &\mu_f \triangle_{yy} \boldsymbol{\kappa}_{\boldsymbol{P}}^{\boldsymbol{j}} - \nabla_y \pi_P^j = -e^j && (j = 1, 2, 3)\\ &\nabla_y \cdot \boldsymbol{\kappa}_{\boldsymbol{P}}^{\boldsymbol{j}} = 0 && \text{in } Y_f \\ &\boldsymbol{\kappa}_{\boldsymbol{P}}^{\boldsymbol{j}} = 0 && \text{on } \partial Y_{fs} \end{aligned} \tag{48}$$

The macroscopic coefficients $\mathbf{K}_{\mathbf{P}}^{\mathbf{eff}}$ and $\mathbf{K}_{\mathbf{E}}^{\mathbf{eff}}$ are nothing but the macroscopic hydraulic and electro-osmotic conductivities (Moyne and Murad 2006a, Moyne and Murad 2006b). It should be noted that, since the closure relation for $\mathbf{K}_{\mathbf{E}}^{\mathbf{eff}}$ contains the zeta potential, by combining the nanoscopic constitutive law (16) for ζ^0 with (47(b)) we can build-up numerically the dependence $\mathbf{K}_{\mathbf{E}}^{\mathbf{eff}} = \mathbf{K}_{\mathbf{E}}^{\mathbf{eff}}(C_{Nab^+}^0, C_{Hb^+}^0)$. This result is of utmost importance as it bridges nanoscopic/microscopic and macroscopic results.

Finally, the macroscopic mass conservation can easily be obtained by averaging (31) using the divergence theorem along with boundary condition (38) to obtain

$$\nabla_x \cdot \mathbf{V}_{\mathbf{D}}^{\mathbf{0}} = \nabla_x \cdot \left(\mathbf{K}_{\mathbf{E}}^{\mathbf{eff}} \nabla_x \phi^0 + \mathbf{K}_{\mathbf{P}}^{\mathbf{eff}} \nabla_x p^0 \right) = 0$$

SUMMARY OF THE THREE SCALE MODEL

We are now ready to formulate our three-scale steady-state problem. Let Ω be the macroscopic domain occupied by the kaolinite saturated by an aqueous solution containing four monovalent ions $\{Na^+, H^+, OH^-, Cl^-\}$. Given the set of constants $\{F, \widetilde{\varepsilon}_0, \widetilde{\varepsilon}_r, \mu_f, D_{Na^+}, D_{Cl^-}\}$, the pair of characteristics functions $\{\mathbf{f}, \boldsymbol{\kappa}_{\boldsymbol{P}}\}$, solution of (45) and (48) and $\{\zeta^0, K_d^0\}$ depending on $\{C_{Hb^+}^0, C_{Nab^+}^0\}$ solution of the nanoscopic problems (16) and (10), find the macroscopic unknowns $\{C_{Nab^+}^0, p^0, \phi^0, \mathbf{V}_{\mathbf{D}}^{\mathbf{0}}\}$ satisfying

$$\left\{ \begin{aligned} &\nabla_x \cdot \mathbf{V}_{\mathbf{D}}^{\mathbf{0}} = 0 \\ &\mathbf{V}_{\mathbf{D}}^{\mathbf{0}} = -\mathbf{K}_{\mathbf{E}}^{\mathbf{eff}} \nabla_x \phi^0 - \mathbf{K}_{\mathbf{P}}^{\mathbf{eff}} \nabla_x p^0 \\ &R^0 \frac{\partial C_{Nab^+}^0}{\partial t} + \nabla_x \cdot \left(C_{Nab^+}^0 \mathbf{V}_{\mathbf{D}}^{\mathbf{0}} \right) = \nabla_x \cdot \left[\mathbf{D}_{\mathbf{Na}^+}^{\mathbf{eff}} \left(\nabla_x C_{Nab^+}^0 + C_{Nab^+}^0 \nabla_x \overline{\phi}^0 \right) \right] \\ &\nabla_x \cdot \left(\mathbf{A}^{\mathbf{eff}} \nabla_x C_{Nab^+}^0 + \mathbf{B}^{\mathbf{eff}} \nabla_x \overline{\phi}^0 \right) = 0 \end{aligned} \right. \tag{49}$$

with the effective parameters $\{\mathbf{K}_{\mathbf{E}}^{\mathbf{eff}}, R^0, \mathbf{B}^{\mathbf{eff}}\}$ depending on $\{C_{Nab^+}^0, C_{Hb^+}^0\}$ solution of the microscopic closure problems

$$\begin{aligned} &\mathbf{K}_{\mathbf{E}}^{\mathbf{eff}} = -\frac{\widetilde{\epsilon}_0 \widetilde{\epsilon}_r \zeta^0}{\mu_f} \langle \mathbf{I} + \nabla_y \mathbf{f} \rangle \qquad \mathbf{K}_{\mathbf{P}}^{\mathbf{eff}} = \langle \boldsymbol{\kappa}_{\boldsymbol{P}} \rangle \qquad R = \eta + \langle K_d^0 \rangle_{fs} \\ &\mathbf{D}_{\mathbf{Na}^+}^{\mathbf{eff}} = D_{Na^+} \langle \mathbf{I} + \nabla_y \mathbf{f}\,(\mathbf{y}) \rangle \qquad \mathbf{A}^{\mathbf{eff}} = F \langle \mathbf{I} + \nabla_y \mathbf{f} \rangle \left(D_{Na^+} - D_{Cl^-} \right) \\ &\mathbf{B}^{\mathbf{eff}} = F \langle \mathbf{I} + \nabla_y \mathbf{f} \rangle \left[\left(D_{Na^+} + D_{Cl^-} \right) C_{Nab^+} + D_{Cl^-} \left(1 - \frac{K_W}{C_{Hb^+}^2} \right) C_{Hb^+} \right]. \end{aligned} \tag{50}$$

In the above three-scale representation of the medium, the geometry of the micropores is described by the characteristic functions $(\mathbf{f}, \boldsymbol{\kappa}_{\boldsymbol{P}})$, whereas the electro-chemistry at the nanoscale is propagated to the macroscale through the relation between the effective coefficients $\{\mathbf{K}_{\mathbf{E}}^{\mathbf{eff}}, R^0\}$ and the nanoscopic ζ^0-potential depending on $\{C_{Nab^+}^0, C_{Hb^+}^0\}$.

NUMERICAL RESULTS

To illustrate the efficiency of the three-scale model in providing numerical predictions of electrokinetic remediation of a kaolinite sample, we numerically solve the one-dimensional version of (49)–(50). We consider a stratified microstructure of the clay composed of parallel particles of face-to-face contact (Fig. 4). In this idealized form of microstructure, the volume averaging is nothing but the transversal averaging in the normal direction to the particle surfaces. Furthermore, since flow and ion transport occur only in the x-direction, we only keep track of the axial components of the fluxes $\{\mathbf{J}^{\mathbf{eff}}_{\mathbf{Na}^+}, \mathbf{I}^{\mathbf{eff}}_{\mathbf{f}}, \mathbf{V}^{\mathbf{0}}_{\mathbf{D}}\}$ and the tensors $\{\mathbf{K}^{\mathbf{eff}}_{\mathbf{E}}, \mathbf{K}^{\mathbf{eff}}_{\mathbf{P}}, \mathbf{D}^{\mathbf{eff}}_{\mathbf{Na}}, \mathbf{A}^{\mathbf{eff}}, \mathbf{B}^{\mathbf{eff}}\}$ denoted herein without boldface. In addition, for conciseness of notation, hereafter we suppress the subscript 0. Under these assumptions, the macroscopic system of differential equations can be rewritten in the form

$$\mathbf{T}\frac{\partial \mathbf{U}(\mathbf{x},t)}{\partial \mathbf{t}} + \frac{\partial}{\partial \mathbf{x}}\left(\mathbf{D}\frac{\partial \mathbf{U}(\mathbf{x},t)}{\partial \mathbf{x}}\right) = 0 \qquad \text{in } \widetilde{\Omega} = [0,L]\times[0,t] \tag{51}$$

with the vector of unknowns $\mathbf{U} := \{C_{Nab^+}, p, \phi\}$ and the tensors

$$\mathbf{T}_{ij} := \begin{cases} -R, & \text{if } i=j=1 \\ 0, & \text{other cases} \end{cases} \qquad \mathbf{D} := \begin{bmatrix} 0 & K_P^{eff} & K_E^{eff} \\ D^{eff}_{Na^+} & K_P^{eff} C_{Nab^+} & \left(K_E^{eff} + \frac{F D^{eff}_{Na^+}}{RT}\right) C_{Nab^+} \\ A & 0 & B^{eff} \end{bmatrix}$$

The macroscopic system (51) is supplemented by initial and boundary conditions. In particular, for the concentration we adopt the Danckwerts' boundary condition at the anode located at $(x = 0)$ along with the absence of diffusive flux at the cathode $(x = L)$. In addition, we prescribe Dirichlet boundary conditions for pressure in both sides and given electric current/potential at the anode/cathode, respectively. We, then, have

$$\begin{cases} p = \overline{p} & \text{at } x = 0, L \\ V_D C_{Nab^+} - D^{eff}_{Na^+}\left(\dfrac{\partial C_{Nab^+}}{\partial x} + C_{Nab^+}\dfrac{\partial \overline{\phi}}{\partial x}\right) = V_D \overline{C} & \text{at } x = 0 \\ -D^{eff}_{Na^+}\left(\dfrac{\partial C_{Nab^+}}{\partial x} + C_{Nab^+}\dfrac{\partial \overline{\phi}}{\partial x}\right) = 0 & \text{at } x = L \\ \left(A^{eff}\dfrac{\partial C_{Nab^+}}{\partial x} + B^{eff}\dfrac{\partial \overline{\phi}}{\partial x}\right) = -I_0 & \text{at } x = 0 \\ \phi = 0 & \text{at } x = L \end{cases} \tag{52}$$

with $\overline{C}$ and I_0 the sodium concentration in the reservoir and given electric current at the anode (see Fig. 4).

FINITE VOLUME METHOD

The discretization of the macroscopic system of EDP's (51)–(52) is performed using the finite volume method (Patankar 1980). The technique consists in decomposing the macroscopic domain into non-overlapping control volumes, each one surrounding a grid point and integrating the conservative form of the governing equations (51) in each volume (see Fig. 5).

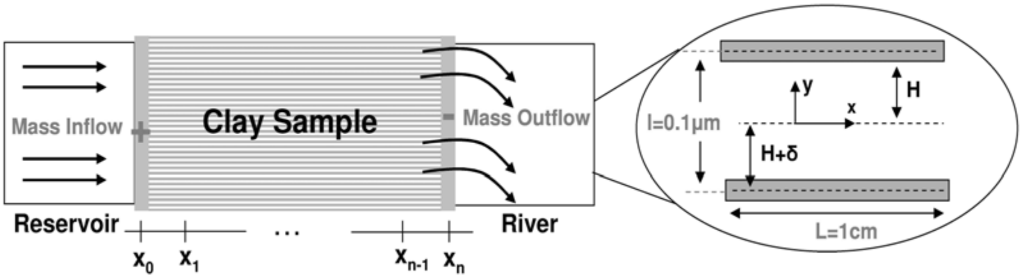


Fig. 4 – Stratified arrangement of face-to-face particles.

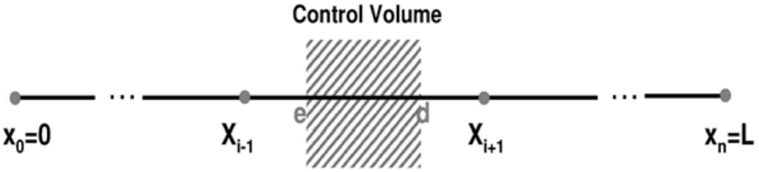


Fig. 5 – Discretization of the domain.

Denoting x_i $(i = 0, 1, ...)$, t_n $(n = 0, 1, ...)$ an uniform partition of the spatial and time domains, with $\triangle x := x_i - x_{i-1}$, $\triangle t := t_n - t_{n-1}$ the mesh size and time step, respectively, we have

$$\int_e^d \int_{t_n}^{t_n+\triangle t} \mathbf{T}\frac{\partial \mathbf{U}}{\partial \mathbf{t}} dtdx + \int_{t_n}^{t_n+\triangle t}\int_e^d \frac{\partial}{\partial \mathbf{x}}\left(\mathbf{D}\frac{\partial \mathbf{U}}{\partial \mathbf{x}}\right) dxdt = 0$$

Boundary conditions are enforced in a similar manner (Patankar 1980). For instance, the transport equation (49(c)) is integrated over the half control volume adjacent to the boundary. In particular, when applying this procedure to the non-linear Danckwerts' boundary condition for the sodium transport (52(b)), we obtain

$$-\int_0^{i=1}\int_t^{t+\triangle t} R\frac{\partial C_{Nab^+}}{\partial t}dtdx + \int_t^{t+\triangle t}\int_0^i \frac{d}{dx}\left(D^{eff}_{Na^+}\frac{dC_{Nab^+}}{dx} + \alpha C_{Nab^+}\right)dxdt$$

$$= -\int_0^{i=1} R^{t+\triangle t}(C^{t+\triangle t}_{Nab^+} - C^t_{Nab^+})dx + \int_t^{t+\triangle t}[(D^{eff}_{Na^+}\frac{dC_{Nab^+}}{dx} + \alpha C_{Nab^+})(i) - V_D\overline{C}]dt = 0$$

with

$$\alpha = K_P^{eff}\frac{\partial p}{\partial x} + \left(K_E^{eff} + \frac{FD^{eff}_{Na^+}}{RT}\right)\frac{\partial \phi}{\partial x}$$

We adopt the classical central difference scheme for the spatial derivatives combined with a linear interpolation in time. Denoting α_i the nodal values of α, it is worth noting that the discrete version of the non-linear boundary condition can be solved for the sodium concentration on the boundary. This yields

$$C^{t+\triangle t}_{Nab^+}(0) = \frac{\left[V\overline{C} - \left(1 + 0.5\alpha_i^{t+\triangle t}\right)C^{t+\triangle t}_{Nab^+}(1) - 0.5R^{t+\triangle t}C^t_{Nab^+}(0)\triangle x^2/\triangle t\right]}{\left(0.5\alpha_i^{t+\triangle t} - 1 - 0.5R^{t+\triangle t}\triangle x^2/\triangle t\right)}.$$

The solution of the above non-linear equation is obtained using Newton's method.

NUMERICAL EXAMPLES

In the numerical simulation of the desalination of a clay sample by elecrokinetics, we adopt the values $D_{Na^+} = 1.334 \times 10^{-9} m^2/s$, $\overline{p} = 10^5 Pa$, $\overline{C} = 1\ mol/m^3$, $I_0 = 1 A/m^2$ along with an initial concentration $C^0_{Nab^+} = 10\ mol/m^3$, time step $\Delta t = 1s$ and an uniform mesh of 500 grid points.

In Figure 6 we display the evolution of the macroscopic unknowns $\{C_{Nab^+},\ p,\ \phi\}$ along with the nanoscopic parameter ζ for $pH = 8.0$. In this basic regime, the ζ-potential is negative, with, magnitude decreasing as the clean-up process evolves (recall Fig. 3). As $\zeta < 0$ the electro-osmotic flow occurs in the same direction of the applied electrical field and leads to gradual desalination of the clay sample, as one may observe in Figure 6(a). Figure 6(b) shows the evolution of the distribution of the electric potential. Since charge conservation (49(d)) gives rise to a strong coupling between the concentration and electric potential distributions, the non-linear profile of the sodium concentration also induces a non-linear behavior of the electric potential. As $t \to \infty$, the electric potential profiles converge to the linear one except in the vicinity of the cathode. The evolution of the pressure is displayed in Figure 6(c). By invoking the mass balance (49(a)), the Darcy velocity is constant and, consequently, a non-linear pressure behavior arises in order to counterbalance the gradient of electric potential.

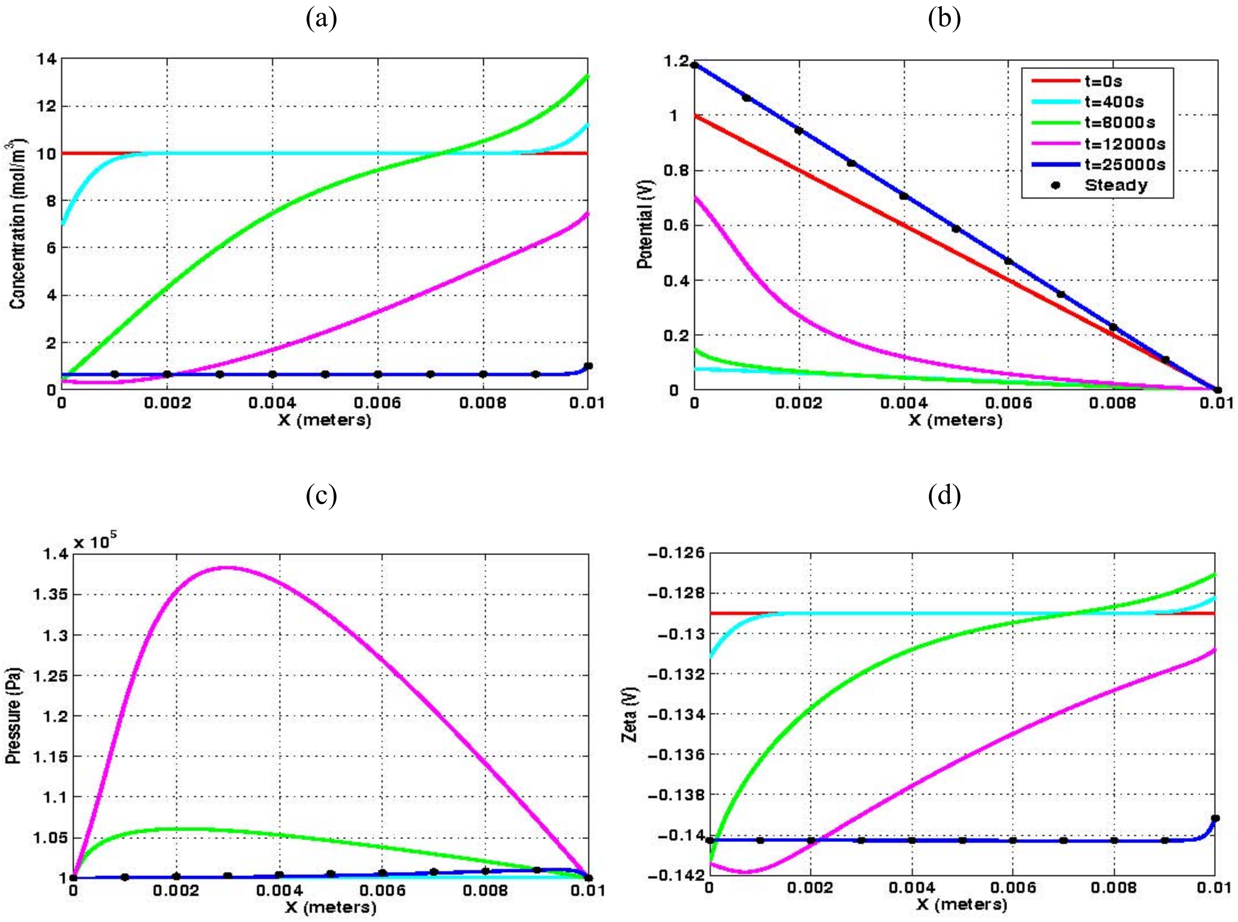


Fig. 6 – Results of the numerical simulations for $pH = 8.0$.

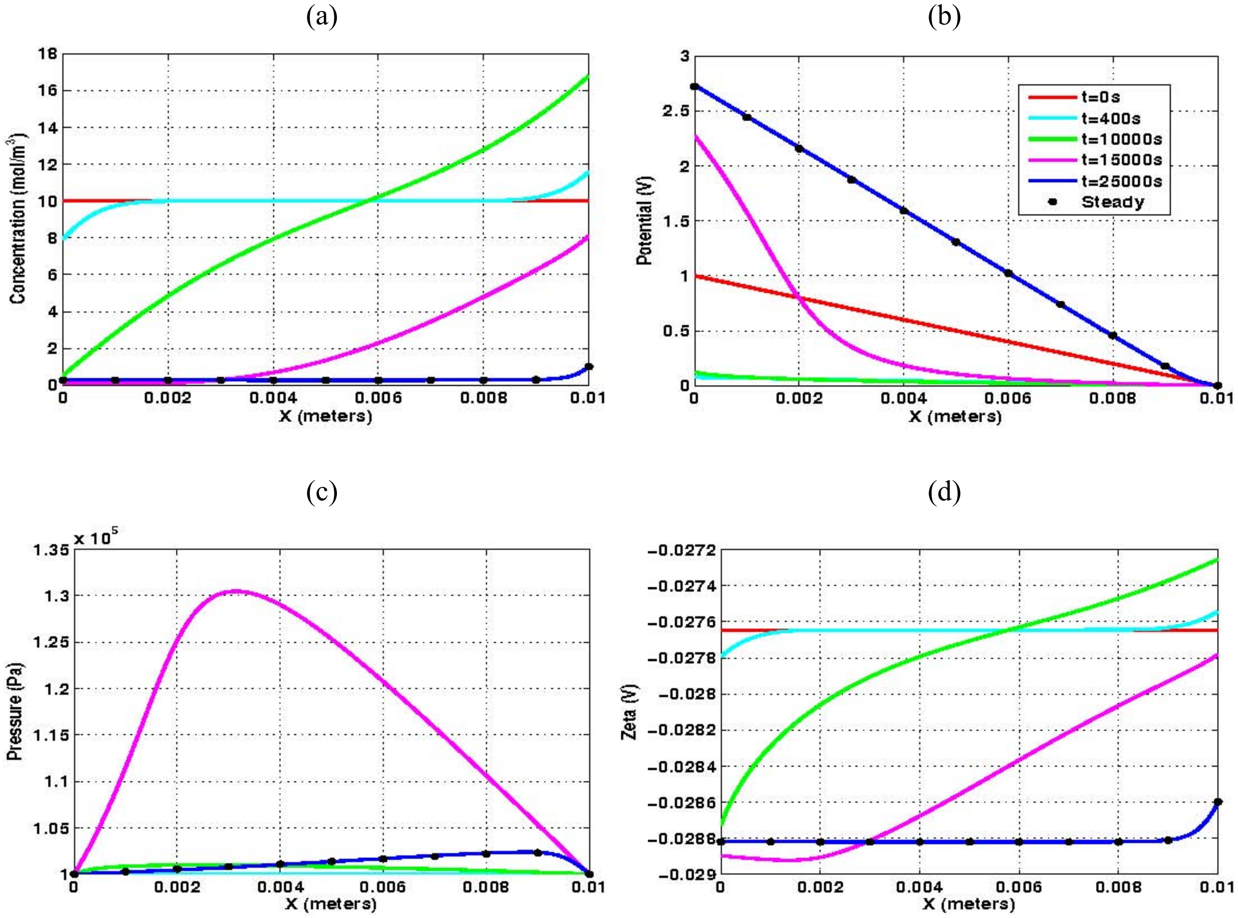

(a) (b) (c) (d)

Fig. 7 – Results of the numerical simulations for $pH = 6.0$.

Finally, in Figure 7, we display the same plots for the lower value $pH = 6$. We may particularly observe, substantial increase in the electric potential towards the anode, which is due to the decrease in the electrical-conductivity B in (20) for a lower pH. To maintain the fixed current I_o at the anode, ϕ has to raise in order to increase the electro-osmotic driving force to counter-balance the decrease in B. In addition, we may observe a more efficient clean-up procedure in Figure 7(a) compared to Figure 6(a).

CONCLUSION

In this paper we built-up a new three-scale model to describe ion transport in Kaolinite clays, including pH influence on adsorption. Effective governing equations were derived by double averaging the nanoscopic behavior of the medium. Among the homogenized results, we highlight the isotherm adsorption for Na^+ concentration, which was rigorously reconstructed from the electrical double layer behavior at the nanoscale. Numerical simulations of a transient electrokinetic remediation experiment were performed to validate the three-scale theory. The model proposed herein consists of a first multiscale attempt at capturing the influence of pH on ion adsorption in clays.

RESUMO

Neste artigo propomos um modelo em três escalas para descrever o acoplamento entre o fluxo eletroosmótico e o transporte de íons incluindo fenômenos de adsorção em uma caulinita. A argila é caracterizada por três escalas nano/micro e macroscópica. A escala microscópica é constituída por micro-poros saturados por uma solução aquosa contendo quatro íons monovalentes e partículas sólidas carregadas eletricamente circundadas por uma dupla camada elétrica fina. O movimento dos íons é governado pelas equações de Nernst-Planck e a influência da dupla camada sobre o fluxo aquoso é modelada por uma condição de contorno de deslizamento da componente tangencial do campo de velocidade (condição de Helmholtz-Smoluchowski). Além disso, uma condição de adsorção na interface fluido-sólido para os íons Na^+ é postulada capturando a retenção do sódio na dupla camada elétrica. O modelo em duas escalas nano/micro incluindo a adsorção do sal e a condição de deslizamento da velocidade é homogeneizado levando a derivação das equações macroscópicas na escala de Darcy. Um dos aspectos inovadores do modelo em três escalas é a reconstrução da lei constitutiva para o coeficiente de partição que governa a adsorção do Na^+ na dupla camada elétrica. Para ilustrar as potencialidades do modelo em três escalas na simulação da eletroremediação de solos argilosos, o modelo macroscópico é discretizado utilizando o método de volumes finitos no intuito de simular a dessalinização de uma amostra de caulinita por técnica de eletrocinética.

Palavras-chave: dupla camada elétrica, eletro-osmose, homogeneização, caulinita, Nernst-Planck, Poisson-Boltzmann.

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