THE SCALE-UP PROBLEM FOR ION TRANSPORT IN KAOLINITE CLAYS INCLUDING PH-DEPENDENCE

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Summary. *We propose a new multiscale computational model to simulate electrokinetic remediation processes in clayey soils. The macroscopic governing equations are derived using the homogenization procedure applied to the pore-scale description consisting of micro-pores saturated by an aqueous solution containing four monovalent ionic species (Na^+, H^+, Cl^-, OH^-) and charged solid particles surrounded by thin electrical double layers. The homogenized equations are discretized by the finite element method and applied to numerically simulate an electroosmosis experiment for decontamination of a clay sample by electrokinetics. Boundary conditions of Dankwerts type are postulated at the electrodes which brings additional complexity to the iterative algorithm for solving the discrete model.*

1 INTRODUCTION

In earlier papers [1, 2] some of the authors have developed new upscaling methods to describe electrochemical phenomena in active clays. Within the framework of homogenization-based approaches the complex effective response of the medium has incorporated pore-scale electro-chemo-mechanical couplings with phenomena such as electro-osmosis, electro-migration and osmotic swelling naturally appearing in the macroscopic forms of the convection-diffusion equations, Darcy's law and modified Terzaghis effective stress principle.

Despite the enormous improvement achieved by multiscale models they were developed for electrolyte solutions composed of two fully dissociated monovalent ions Na^+ and Cl^- and constant $pH = 7$. Consequently the transport of H^+ and OH^- ions along with chemical protonation/deprotonation reactions between the H^+ ions and surface charged groups lying on the clay particle surface leading to pH-dependency were neglected. First attempts at incorporating pH effects within the framework of homogenization were pursued by the authors in [3, 4]. Numerical approximations of the resultant multiscale model were carried-out and applied to computationally simulate the one-dimensional electro-osmotic experiment with Dirichlet boundary conditions enforced at the electrodes. In this work we generalize these simulations to incorporate more realistic boundary condition of Danckwerts type at the electrodes [5]. The assessment of the numerical results obtained
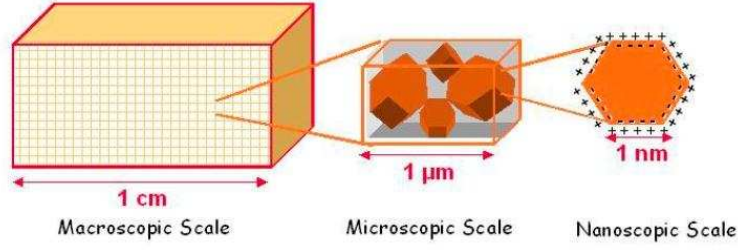
Figure 1: Macroscopic, microscopic and nanoscopic portraits in Kaolinite

within this new computational model is performed through a perturbation-based approach which gives rise to semi-analytical solutions of the electro-osmosis experiment capable of establishing accurate scenarios of electro-kinetic remediation of clayey soils.

2   REVIEW OF THE MULTISCALE MODEL

We begin by reviewing the three-scale electro-chemical model (Fig.1) proposed in [3, 4] incorporating pH-effects. Let $\Omega = \Omega_s \cup \Omega_f \subset \Re^3$ be the microscopic domain occupied by a biphasic porous media composed of clay particles and micro-pores filled by a bulk fluid, and Γ_{fs} the solid / fluid interface. The hydrodynamics is governed by the classical Stokes problem

$$\nabla \cdot \mathbf{v} = 0, \quad \mu_f \triangle \mathbf{v} - \nabla p = 0 \qquad \text{in } \Omega_f \tag{1}$$

where $\mathbf{v}$ is the fluid velocity, p the pressure and μ_f the water viscosity. The steady state movement of the four ionic species with concentrations C_i ($i = (Na^+, H^+, Cl^-, OH^-)$ is governed by the Nernst-Planck equations

$$\nabla \cdot (C_{ib}\mathbf{v}) - \nabla \cdot \left[D_i \left(\nabla C_{ib} + C_{ib}\nabla \overline{\phi} \right) \right] + \dot{m} = 0, \quad \left(\dot{m} = 0 \text{ for } i = Na^+, Cl^- \right) \qquad \text{in } \Omega_f \tag{2}$$

where D_i are the binary water-ion diffusion coefficients, $\overline{\phi} := F\phi/RT$ the dimensionless microscopic electrical potential with $\{F, R, T\}$ the set composed of Faraday constant, universal ideal gas constant and absolute temperature and $\dot{m}$ a source term that quantifies the mass production of H^+ and OH^- due to water hydrolysis.

To close our microscopic model it remains to postulate boundary conditions on the particle/micropore interface Γ_{fs}. Consider that the normal component of velocity and electro-diffusive ion fluxes vanish on Γ_{fs}. In addition, owing to the presence of the thin electrical double layer surrounding the particles we postulate the so-called Smoluchowsky slip [2] wherein the tangential velocity exhibits a discontinuity at the interface. Denoting and $\boldsymbol{\tau}$ the unitary tangential vector at Γ_{fs} we have

$$\mathbf{v} \cdot \boldsymbol{\tau} = \widetilde{\epsilon}_0 \widetilde{\epsilon}_r \mu_f^{-1} \zeta \nabla \phi \cdot \boldsymbol{\tau} \qquad \text{on } \Gamma_{fs} \tag{3}$$

where $\widetilde{\epsilon}_0$ is the permittivity of the free space, $\widetilde{\epsilon}_r$ is the dielectric constant of the solvent and ζ the zeta potential. To close the microscopic model we need to build-up the constitutive law of the ζ-potential

in terms of pH and salinity. To this end we make we proceed within the framework of the electrical double layer theory with a nonlinear surface charge density due to protonation / deprotonation chemical reactions. This yields a single algebraic equation for the ζ-potential whcih has been solved in [3, 4]

The numerical constitutive response $\zeta = \zeta(C_{Nab^+}, C_{H^+})$ is depicted in (Fig.2). We may note strong dependence of the ζ-potential on the pH in a nearly skew-symmetric fashion around the point of zero charge (isoelectric point) $pH = 5.5$.
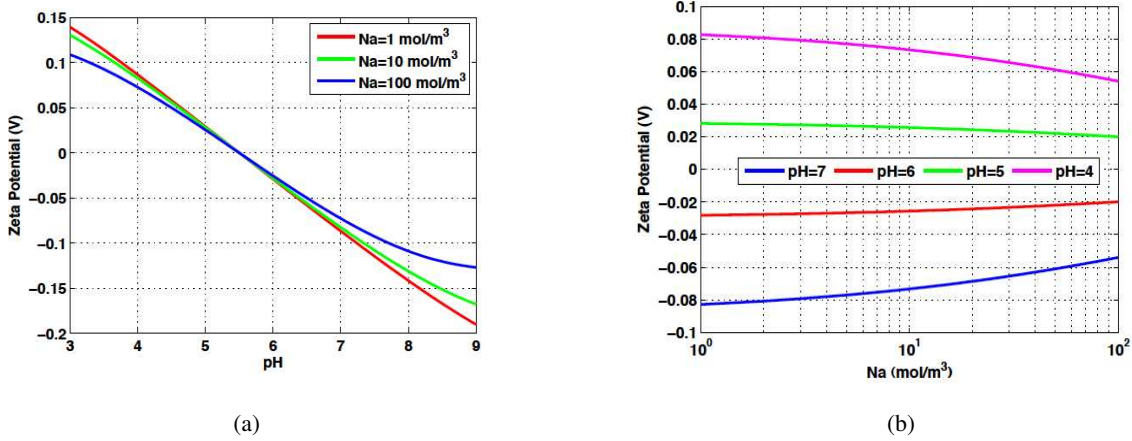

(a) (b)

Figure 2: Constitutive Response of the ζ-Potential as a Function of pH and C_{Nab^+}.

Application of the a formal homogenization procedure to the pore-scale model leads to the macroscopic equations [3]

$$
\begin{cases}
\nabla \cdot \mathbf{V_D} = \nabla \cdot [-K_P \nabla p - K_E \nabla \phi] = 0 \\
\nabla \cdot \mathbf{J_{Na^+}} = \nabla \cdot \left[C_{Na^+} \mathbf{V_D} - D_{Na^+} \left(\nabla C_{Na^+} + C_{Na^+} \nabla \overline{\phi} \right) \right] = 0 \\
\nabla \cdot \mathbf{J_{H^+}} = \nabla \cdot \left[\Theta C_{H^+} \mathbf{V_D} - \widehat{D}_{H^+} \left(\nabla_x C_{H^+} + C_{H^+} \nabla \overline{\phi} \right) \right] = 0 \\
\nabla \cdot \mathbf{I_f} = \nabla \cdot \left[A \nabla C_{Nab^+} + B \nabla C_{Hb^+} + C \nabla \overline{\phi} \right] = 0
\end{cases}
\tag{4}
$$

where $\mathbf{V_D}$ the Darcy velocity, (K_P, K_E) the hydraulic and electroosmotic permeability, $(\mathbf{J_{Na^+}}, \mathbf{J_{H^+}})$ the convective/electro-diffusive ionic fluxes, $(\Theta, \widehat{D}_{H^+})$ nonlinear coefficients given by $\Theta := 1 - K_W/C_{Hb^+}^2$ and $\widehat{D}_{H^+} := D_{H^+} + D_{OH^-} K_W/C_{Hb^+}^2$, $\mathbf{I_f}$ the electric current, C the electrical conductivity and (A, B) the coupling coefficients for the current [3, 4]. The electroomsotic permeability is nothing but the average of the ζ-potential and theerfore inherits its constitutive behavior.

3 APPLICATION TO AN ELECTROOSMOSIS EXPERIMENT

The macroscopic system is discretized by finite elements and applied to simulate an electroosmosis experiment. An anode and a cathode are placed at the positions $x = 0$ and $x = L$ respectively. Denoting $C_{Na^+}^{ref}, C_{H^+}^{ref}$ the sodium and H^+ concentration in the reservoir in the anode compartment and I_0 a given electric current postulate Danckwerts' boundary conditions at the elctrodes [5]

3

$$\mathbf{J_{Na^+}}|_{x=0} = C_{Na^+}^{ref} \mathbf{V_D} \qquad\qquad \mathbf{J_{Na^+}}|_{x=L} = C_{Na^+} \mathbf{V_D}$$

$$\mathbf{J_{H^+}}|_{x=0} = \Theta C_{H^+}^{ref} \mathbf{V_D} + I_0 F^{-1} \qquad \mathbf{J_{H^+}}|_{x=L} = \Theta C_{H^+} \mathbf{V_D} + I_0 F^{-1} \qquad (5)$$
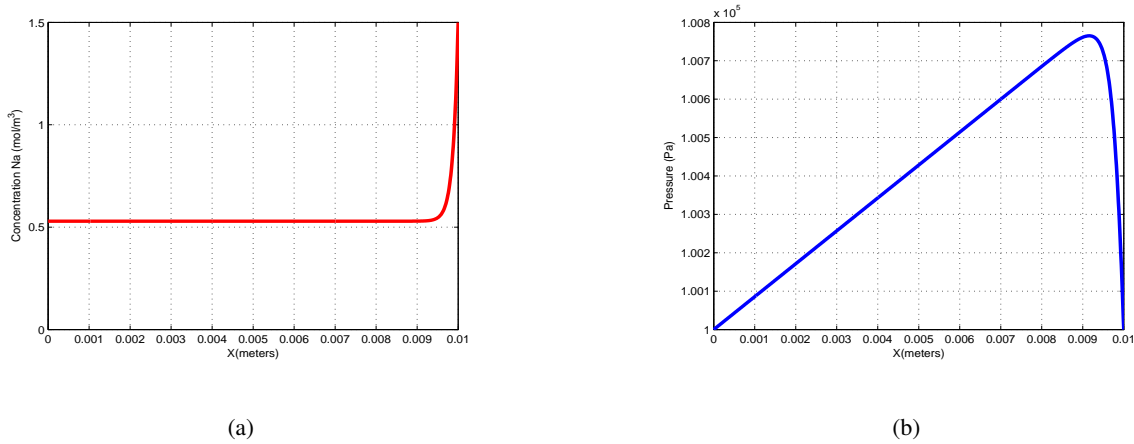

(a)

(b)

Figure 3: Sodium and pore pressure steady state profiles

In Fig. 3 we display the sodium concentration and pressure profiles. In contrast to the case of Dirichlet boundary condition presented in [3], the enforcement of (5) leads to a plateau $C_{Na^+}^{plateau}$ (whose value $\mathbf{J_{Na^+}}/\mathbf{V_D}$ can be estimated from perturbation analysis) coupled with a sharp layer in the vicinity of the cathode. In addition, the pressure gradient changes sign to fulfill the incompressibility constraint. The more realistic simulation presented herein can be further explored to construct reliable electrokinetic remediation scenarios.

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