A three-scale model for ionic solute transport in swelling clays incorporating ion–ion correlation effects

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ABSTRACT

A new three-scale model is proposed to describe the movement of ionic species of different valences in swelling clays characterized by three separate length scales (nano, micro, and macro) and two levels of porosity (nano- and micropores). At the finest (nano) scale the medium is treated as charged clay particles saturated by aqueous electrolyte solution containing monovalent and divalent ions forming the electrical double layer. A new constitutive law is constructed for the disjoining pressure based on the numerical resolution of non-local problem at the nanoscale which, in contrast to the Poisson–Boltzmann theory for point charge ions, is capable of capturing the short-range interactions between the ions due to their finite size. At the intermediate scale (microscale), the two-phase homogenized particle/electrolyte solution system is represented by swollen clay clusters (or aggregates) with the nanoscale disjoining pressure incorporated in a modified form of Terzaghi's effective principle. At the macroscale, the electro-chemical–mechanical couplings within clay clusters is homogenized with the ion transport in the bulk fluid lying in the micro pores. The resultant macroscopic picture is governed by a three-scale model wherein ion transport takes place in the bulk solution strongly coupled with the mechanics of the clay clusters which play the role of sources/sinks of mass to the bulk fluid associated with ion adsorption/desorption in the electrical double layer at the nanoscale. Within the context of the quasi-steady version of the multiscale model, wherein the electrolyte solution in the nanopores is assumed at instantaneous thermodynamic equilibrium with the bulk fluid in the micropores, we build-up numerically the ion-adsorption isotherms along with the constitutive law of the retardation coefficients of monovalent and divalent ions. In addition, the constitutive law for the macroscopic swelling pressure is reconstructed numerically showing patterns of attractive forces between particles for bivalent ions for particular ranges of bulk concentrations. The three-scale model is applied to numerically simulate ion diffusion in a compacted clay liner underneath a sanitary landfill. Owing to the distinct constitutive behavior of the swelling pressure and partition coefficient for each ionic species, different compaction regimes and diffusion/adsorption patterns, with totally different characteristic time scales, are observed for sodium and calcium migration in the clay liner.

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1. Introduction

The adequate design of engineered barriers for waste containment to fulfill environmental regulations involves optimization of the performance of surface caps and subsurface liners to ensure minimization of pollutant migration to the subsurface. Such issue remains very relevant as society continue to generate large amounts of hazardous waste requiring efficient long-term storage to the solid waste containment industry. Hydrated swelling clays have been widely adopted as buffer materials in geoenvironmental engineering playing a key rule in engineered liner systems in municipal solid waste landfills, mining waste containment facilities and seals for high-level long lived radioactive waste disposal sites. Owing to the self-sealing capability arising from the expandable lattice along with large specific surface area, high chemical capacity for adsorption of contaminants and low permeability, compacted clays such as bentonite possess effective barrier properties for isolation of wastes from the surrounding environment [28].

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Latin symbols

$\boldsymbol{E}$	electric field
$\boldsymbol{I}$	identity tensor
$\boldsymbol{I}_e$	electric current in the clusters
$\boldsymbol{I}_f$	electric current in the micropores
$\boldsymbol{J}$	total molar flux density in the micropores
$\boldsymbol{j}$	total molar flux density in the clusters
$\boldsymbol{j}_d$	diffusive flux in the clusters
$\boldsymbol{J}_{fd}$	diffusive flux in the micropores
$\mathbf{n}$	unit outward normal to the solid
$\boldsymbol{r}, \boldsymbol{R}$	position vector
$\mathbf{u}$	displacement vector
$\boldsymbol{V}_f$	liquid velocity in the micropores
$\boldsymbol{V}_{fs}$	liquid velocity in the micropores relative to solid
$\mathbf{v}_D$	Darcy's velocity in the clusters
c_i	concentration in the clusters of component i
C_i	concentration in the micropores of component i
c	direct correlation function
d	ion diameter
$\mathcal{D}_i$	microscopic diffusion coefficient of component i
$\boldsymbol{D}_i$	macroscopic diffusion coefficient of component i
E	Young modulus
G_i	partition coefficient of component i
g	correlation function
h	$g - 1$
k	Hankel variable
k_B	Boltzmann's constant
n_f	macroscopic volume fraction
p_b	bulk pressure
P_f	fluid pressure
q_i	ionic charge of component i
R	perfect gas constant
R_i	retardation coefficient of component i
T	temperature
U_N	intermolecular potential
u_{ij}	intermolecular potential between ions i and j
u_{ij}^{HS}	hard sphere contribution of intermolecular potential between ions i and j

v_i^{hs}	short-range exterior potential
y	$h - c$
Y	unit cell
Y_f	domain occupied by fluid in an unit cell
Y_s	domain occupied by solid in an unit cell
∂Y_{fs}	interface solid/fluid in an unit cell

Greek symbols

$\boldsymbol{\Pi}_d$	disjoining stress
$\boldsymbol{\sigma}_f$	stress tensor of bulk fluid
$\boldsymbol{\sigma}_t$	total stress in the clusters
$\boldsymbol{\sigma}_U$	intermolecular stress tensor
$\boldsymbol{\sigma}_K$	kinetic component for ideal gas
$\boldsymbol{\sigma}_{el}$	intermolecular stress tensor due to electrostatic forces
$\boldsymbol{\sigma}_{core}$	intermolecular stress tensor due to hard sphere interaction
$\boldsymbol{\sigma}_V^{hs}$	exterior stress tensor for ion/hard surface interaction
$\boldsymbol{\nabla}\cdot$	divergence
$\boldsymbol{\nabla}$	gradient
γ_i	activity coefficient of component i
Γ_{fs}	interface solid/liquid
ϵ	permittivity
ε	small parameter of homogenization method
Λ	De Broglie thermal wavelength
μ	chemical potential
ξ	Onsager's parameter
π_b	bulk osmotic pressure
σ	surface charge
$\boldsymbol{\tau}_M$	Maxwell tensor
ϕ	porosity of the cluster
Φ	electrical potential
ψ	electrical potential relative to the bulk
Ω_f	domain occupied by the fluid
Ω_s	domain occupied by the solid

Bentonite is a highly reactive clay frequently used as an important component in geosynthetic clay liners (GCLs) and covers. The efficiency of the clay buffer is strongly dictated by the physicochemical interactions between the leachate that emanates from the wastes and the pore fluid. Since the hydraulic performance of the GCL is controlled by the swelling ability of the bentonite for a given confining pressure, the direct exposure of the GCL to leachate exerts considerable alterations in the geotechnical properties of the liner affecting hydraulic performance causing instability problems which may decrease the service life of the liner and shorten the time of leachate migration to the groundwater system [29].

The avoidance of the deterioration of the landfill liner system caused by perturbations in the shrink–swell behavior of active clays in response to changes in the chemistry of the pore fluid gives rise to important challenges for the development of accurate multiscale models to treat properly the complex electro-chemo-mechanical coupled phenomena at different spatial and temporal scales. In previous works [20–25] the authors have developed two-scale models [22,23] for single porosity swelling porous media characterized by electrically charged surfaces in nanopores saturated by electrolyte solutions with counter- and co-ions. Furthermore such theory was extended to three-scale models of dual porosity type for clays characterized by three separate-length scales (nano, micro and macro) and two levels of porosity [25] (nano- and micropores) (Fig. 1). An essential feature underlying multiscale models is the

bridging between the macroscopic response of the medium and the nanoscopic electro-chemistry in the nanopores. In such context, it becomes mandatory to construct, improve and up-scale properly nanopore scale models to increase reliability in the description of the effective behavior of the swelling system.

The nanoscopic description aims at capturing the interaction between the confined electrolyte solution and charged macromolecules. Such complex description consists of one of the oldest problems studied in electro-chemistry remaining an active area of research with potential applications in a wide variety of areas [2]. When dissolved in a polar solvent, such as water, the macromolecular surfaces acquire a surface charge through the
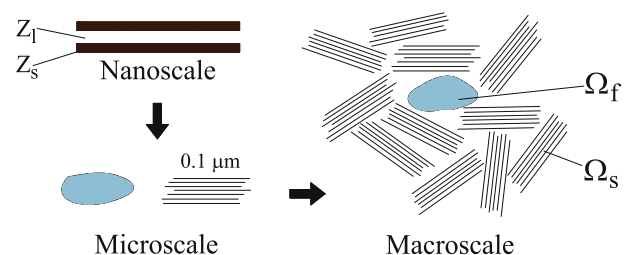

Fig. 1. Natural length scales in a swelling clay.