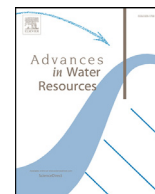




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Transport of water and ions in partially water-saturated porous media. Part 1. Constitutive equations

A. Revil*

ISTerre, CNRS, UMR 5275, Université de Savoie Mont-Blanc, 73376 Le Bourget du Lac, France

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ABSTRACT

I developed a model of cross-coupled flow in partially saturated porous media based on electrokinetic coupling including the effect of ion filtration (normal and reverse osmosis) and the multi-component nature of the pore water (wetting) phase. The model also handles diffusion and membrane polarization but is valid only for saturations above the irreducible water saturation. I start with the local Nernst–Planck and Stokes equations and I use a volume-averaging procedure to obtain the generalized Ohm, Fick, and Darcy equations with cross-coupling terms at the scale of a representative elementary volume of the porous rock. These coupling terms obey Onsager's reciprocity, which is a required condition, at the macroscale, to keep the total dissipation function of the system positive. Rather than writing the electrokinetic terms in terms of zeta potential (the double layer electrical potential on the slipping plane located in the pore water), I developed the model in terms of an effective charge density dragged by the flow of the pore water. This effective charge density is found to be strongly controlled by the permeability and the water saturation. I also developed an electrical conductivity equation including the effect of saturation on both bulk and surface conductivities, the surface conductivity being associated with electromigration in the electrical diffuse layer coating the grains. This surface conductivity depends on the CEC of the porous material.

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1. Introduction

A lot of work has been done modeling of solute transport in porous media (for instance [15,77]) but coupling effects, especially those associated with the charged nature of some solutes and the charged nature of organic matter and clay minerals in soils have been usually neglected. At the scale of a representative elementary volume (REV) of a porous rock, the general constitutive equations describing the flow of electrical charges, ions, and the flow of the water molecules, namely Ohm's, Fick's, and Darcy's laws, are all coupled in the form of a generalized constitutive equation with cross-coupling effects. These couplings are mostly electrokinetic in nature (i.e., associated with the relative displacement of the electrical diffuse layer with respect to the mineral skeleton) and strongly controlled by cation exchange processes on the mineral surface [78–80]. These electrokinetic effects result from the presence of the electrical diffuse layer coating the surface of the grains, especially clay minerals and organic matter that are so important in soils (e.g., [4,82,84,85]). Electrokinetic coupling effects associated with the flow of the pore water in porous media in-

clude (1) the streaming electrical current density associated with the flow of the pore water (or a pore fluid pressure gradient including the effect of the osmotic pressure, e.g., [47]), (2) the electroosmotic coupling associated with the flow of the pore water in response to an electrical current (or an electrical field) (e.g., [69]), and (3) reverse osmosis in charged membrane (e.g., [73]). The material properties entering the coupled constitutive equations can be related to textural properties of the porous material, the properties of the pore fluid, and the electrochemical properties of the interface between the pore water and the minerals such as the zeta potential [47,85] or the excess charge per unit pore volume [32].

The form of the constitutive equations can be obtained from non-equilibrium thermodynamics and the macroscopic material properties described in terms of phenomenological laws (for instance [94]). Alternatively, upscaling can be performed starting with the microscopic (local) equations in order to obtain explicit relationships connecting the macroscopic physical properties to textural and electrochemical parameters (e.g., [2] and references therein). However, and very unfortunately, most of the existing approaches like the one developed by Allaire et al. [2] do not allow to define textural variables at the macroscopic level that can be easily measured to unify material properties into a single model.

* Tel.: +33 479758715.

E-mail address: Andre.Revil@univ-smb.fr, altair256@hotmail.fr

Nomenclature

Variable Meaning

A	Surface area cross-section of the porous material (m^2)
b_i	Mobility for diffusion of species i in the pore water ($\text{m}^2 \text{s}^{-1} \text{J}^{-1}$)
C	Streaming potential coupling coefficient (V Pa^{-1})
CEC	Cation exchange capacity (C kg^{-1})
c_i	Concentration of species i per unit pore volume (m^{-3})
c_i^S	Concentration of i per unit volume of solid due to the diffuse layer (m^{-3})
c_w	Concentration of water molecules (m^{-3})
D	Dissipation per unit volume of the porous material (W m^{-3})
D_i	Diffusivity of species i in the pore water ($\text{m}^2 \text{s}^{-1}$)
E	Macroscopic electrical field (V m^{-1})
e_ξ	Local electrical field in phase ξ (solid, water, fluid) (V m^{-1})
$\hat{n}_{\xi\sigma}$	Unit vector between phases ξ and σ directed from ξ to σ
f	Partition coefficient between the Stern and diffuse layers
F	Electrical formation factor
g	Normalized velocity in the Stokes problem (m^2)
g	Acceleration of the gravity field (m s^{-2})
H	Thickness of the representative elementary volume (M)
j_i	Local flux density of solute i in the pore water phase ($\text{m}^{-2} \text{s}^{-1}$)
j_s	Local current density along the surface of the grains (A m^{-2})
j_w	Local current density in the pore water (A m^{-2})
J	Macroscopic total current density (A m^{-2})
J_d	Macroscopic diffusion flux of the salt ($\text{m}^{-2} \text{s}^{-1}$)
J_i	Macroscopic flux of the ionic species ($\text{m}^{-2} \text{s}^{-1}$)
J_w	Flux of the solvent (the water molecules) ($\text{m}^{-2} \text{s}^{-1}$)
J_c	Macroscopic conduction current density (A m^{-2})
J_D	Macroscopic diffusional current density (A m^{-2})
J_S	Macroscopic streaming current density (A m^{-2})
k_b	Boltzmann constant, $1.3806503 \times 10^{-23}$ ($\text{m}^2 \text{kg s}^{-2} \text{K}^{-1}$)
k_w	Permeability at partial saturation (m^2)
k_S	Permeability at full saturation (m^2)
L	Matrix of material properties (variable)
L_{ij}	Components (ij) of the matrix L (variable)
m	First (porosity) Archie exponent
n	Second (saturation) Archie exponent
n_i	Concentration of species i per unit volume of the porous material (Mol m^{-3})
N	Number of ionic species
p_w	Mechanic pore water pressure (Pa)
p_c	Capillary pressure (Pa)
P	Macroscopic pressure field gradient for the water phase (Pa m^{-1})
\hat{Q}_V	Effective charge density dragged by the pore water flow (C m^{-3})
\hat{Q}_V^S	Value of \hat{Q}_V at saturation (C m^{-3})
Q_V	Total charge density of the diffuse and Stern layers per unit pore volume (C m^{-2})
\bar{Q}_V	Total charge density of the diffuse layer per unit pore volume (C m^{-2})

Q_d	Equivalent surface charge density of the diffuse layer (C m^{-2})
Q_i	Contribution of species i to the surface charge density of the diffuse layer (C m^{-2})
q_i	Charge of species i (C)
Q_S	Source of entropy ($\text{W K}^{-1} \text{m}^{-3}$)
S	Entropy flux through the porous material ($\text{W m}^{-2} \text{K}^{-1}$)
S	Entropy of the porous body ($\text{J m}^{-3} \text{K}^{-1}$)
s_w	Water saturation
S	Surface area of the pore water interface (m^2)
S_{Sp}	Specific surface area ($\text{m}^2 \text{kg}^{-1}$)
T	Absolute temperature (K)
t	Time (S)
T_i	Macroscopic Hittorf number of species i
t_i^w	Hittorf number of species i in the bulk pore water
t_i^S	Hittorf number of species i in the diffuse layer
u	Internal energy of the porous body per unit volume (J m^{-3})
\dot{u}_i	Local velocity of solute i in the pore water (m s^{-1})
\dot{u}_i^m	Mechanical contribution to \dot{u}_i (m s^{-1})
\dot{u}_i^e	Electrical contribution to \dot{u}_i (m s^{-1})
\dot{u}_i^c	Chemical contribution to \dot{u}_i (m s^{-1})
\dot{u}_w	Pore water velocity (m s^{-1})
\dot{u}_w^m	Mechanically-driven pore water velocity (m s^{-1})
\dot{u}_w^e	Electrically-driven pore water velocity (m s^{-1})
\dot{u}_w^c	Osmotically-driven pore water velocity (m s^{-1})
V_p	Pore volume (m^3)
V_ξ	Volume of phase ξ (m^3)
V	Volume of the porous material (m^3)
W	Flux of internal energy (W m^{-2})
\hat{w}	Darcy velocity (m s^{-1})
z	Local distance in the direction of the macroscopic fields (m)
Z	Unit vector in the z -direction
Z	Elevation head from a datum (e.g., the sea level) (m)
ϕ	Connected porosity
α	Tortuosity of the pore space
β_i	Mobility for electromigration of species i ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$)
$\beta_{(+)}$	Equivalent mobility of the counterions of the diffuse layer ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$)
ϵ_w	Dielectric constant of the pore water (F m^{-1})
μ_i	Chemical potential of species i (J)
$\tilde{\mu}_i$	i (J)
μ_i^0	Chemical potential of species i in the reference state (J)
μ_f	Chemical potential of the salt (J)
σ_S	Surface conductivity (S m^{-1})
σ_s	Equivalent conductivity of the solid phase (grains) (S m^{-1})
σ_w	Conductivity of the pore water (S m^{-1})
Γ_ξ	Normalized electric potential in phase ξ in the Laplace problem (m)
$\bar{\Psi}$	Pressure head (m)
φ	Electrical potential (V)
ρ_s	Mass density of the solid (kg m^{-3})
ρ_w	Mass density of the pore water (kg m^{-3})
$\tilde{\rho}$	Local charge density in the pore water (diffuse layer included) (C m^{-3})
π	Osmotic pressure in the pore space (Pa)
η_w	Dynamic viscosity of the pore water phase (Pa s)

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