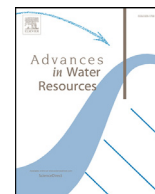




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Transport of water and ions in partially water-saturated porous media. Part 2. Filtration effects

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ABSTRACT

A new set of constitutive equations describing the transport of the ions and water through charged porous media and considering the effect of ion filtration is applied to the problem of reverse osmosis and diffusion of a salt. Starting with the constitutive equations derived in Paper 1, I first determine specific formula for the osmotic coefficient and effective diffusion coefficient of a binary symmetric 1:1 salt (such as KCl or NaCl) as a function of a dimensionless number Θ corresponding to the ratio between the cation exchange capacity (CEC) and the salinity. The modeling is first carried with the Donnan model used to describe the concentrations of the charge carriers in the pore water phase. Then a new model is developed in the thin double layer approximation to determine these concentrations. These models provide explicit relationships between the concentration of the ionic species in the pore space and those in a neutral reservoir in local equilibrium with the pore space and the CEC. The case of reverse osmosis and diffusion coefficient are analyzed in details for the case of saturated and partially saturated porous materials. Comparisons are done with experimental data from the literature obtained on bentonite. The model predicts correctly the influence of salinity (including membrane behavior at high salinities), porosity, cation type (K^+ versus Na^+), and water saturation on the osmotic coefficient. It also correctly predicts the dependence of the diffusion coefficient of the salt with the salinity.

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1. Introduction

The existence of cross-coupling effects in the transport equations of porous media has been observed in the 19th century (e.g., Reuss, 1909; Quincke, 1959). Since these first observations, a rich literature has emerged regarding the modeling of the cross-coupling effects in charged porous media. The fundamental aspects of some of the cross-coupling terms such as electro-osmosis was for instance developed by Gray and Mitchell (1967) driven by some applications in soil sciences and geo-mechanics and later on by microfluidics (e.g., Ghosal, 2010). Hanshaw and Coplen (1973) developed a theory of reverse osmosis based on the concept of excess of charge in the pore space of clayey materials. Revil and Leroy (2004), Revil et al. (2005), and Leroy et al. (2006) developed a consistent theory for transport mechanism in saturated conditions in clayey materials accounting for the partition between the Stern and diffuse layer coating the surface of the clay minerals. This type of approach is complementary to molecular modeling that can be used to compute ionic transport in the interlayer of smectite (Birgersson and Karnland, 2009). Recently, Dominijanni and Manassero (2012) and Dominijanni et al. (2013) developed a complete

theory in which the transport equations with coupling terms were developed in a hydromechanical framework including elastic and plastic deformations. The list of works on this subject is far from being exhaustive and the interested readers could also consult scientific papers dealing with osmotic effects in cells, bones, and the tendons of living beings (e.g., Masic et al., 2016).

In the previous paper of this series (Revil, 2016), I have developed a model describing the generalized constitutive equations of transport of water and ions in the case of a partially saturated charged porous medium and in a rigid skeleton. In this model, the water phase is considered to be the wetting phase (index w) for the solid grains and the non-wetting phase (air) is considered to be very compressible and electrically insulating. By charged porous materials, I mean that the interface between the solid phase and the pore water phase contains an electrical double layer coating the surface of the grains as for instance in soils (Sposito 1991; Sposito et al., 1999; Sposito, 2008) and in consolidated rocks made of silicates and aluminosilicates (e.g., Loret et al., 2002). This electrical double layer includes a Gouy-Chapman diffuse layer of counterions and co-ions (with concentrations usually described by Poisson-Boltzmann distributions, see Gouy, 1910; Chapman, 1913) and a Stern layer of sorbed counterions (see Stern, 1924; Avena and de Pauli, 1998; Leroy and Revil, 2004). The air-water interface can also be the setting of such an electrical double layer (e.g.,

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Nomenclature

Variable Meaning Unit

C	Streaming potential coupling coefficient, V Pa^{-1}
CEC	Cation exchange capacity, C kg^{-1}
$c_{(\pm)}$	Concentration in the reservoir, m^{-3}
$\tilde{c}_{(\pm)}$	Concentration in the pore space, m^{-3}
c_w	Concentration of water in the reservoir, m^{-3}
\tilde{c}_w	Concentration of water in the pore space, m^{-3}
c_f	Mean salinity in the reservoir, m^{-3}
\tilde{c}_f	Mean salinity in the pore water, m^{-3}
\bar{C}, C	Gradient of the chemical potential of the electrolyte (driving force), J m^{-1}
D	Diffusion coefficient of the salt in the porous material, $\text{m}^2 \text{s}^{-1}$
D_f	Diffusion coefficient of the salt in the reservoir, $\text{m}^2 \text{s}^{-1}$
\bar{E}, E	Macroscopic electrical field (driving force), V m^{-1}
e	Elementary charge, 1.6×10^{-19} , C
f	Partition coefficient between the Stern and diffuse layers, -
F	Electrical formation factor, -
J	Macroscopic total current density, A m^{-2}
J_d	Macroscopic diffusion flux of the salt, $\text{m}^{-2} \text{s}^{-1}$
$J_{(\pm)}$	Macroscopic flux of the cations and anions, $\text{m}^{-2} \text{s}^{-1}$
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_r	Relative permeability ($0 \leq k_r \leq 1$), -
k_S	Permeability at saturation, m^2
L	Matrix of material properties, variable
L_{ij}	Components of the matrix L , variable
m	First (porosity) Archie exponent, -
n	Second (saturation) Archie exponent, -
N	Number of ionic species, -
p_w	Mechanical pore water pressure in the reservoir, Pa
\bar{p}_w	Mechanical pore water pressure in the pore water phase, Pa
p_c	Capillary pressure at the representative elementary volume, Pa
\bar{P}, P	Macroscopic pressure gradient (driving force), 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 per unit volume of the pore water phase, C m^{-2}
\bar{Q}_V	Total charge density of the diffuse layer per unit pore volume, C m^{-2}
\bar{Q}_V^S	Value of \bar{Q}_V at saturation, C m^{-2}
s_w	Water saturation, -
s_r	Irreducible water saturation, -
s_e	Effective water saturation, -
S_{Sp}	Specific surface area, $\text{m}^2 \text{kg}^{-1}$
T	Absolute temperature, K
$T_{(\pm)}$	Macroscopic Hittorf number of the cations and anions, -
$t_{(\pm)}^w$	Hittorf number of cations and anions in the reservoirs, -
\hat{w}	Darcy velocity, m s^{-1}
ϕ	Connected porosity, -
$\beta_{(\pm)}$	Mobility in the bulk pore water, $\text{m}^2 \text{s}^{-1} \text{V}^{-1}$
ε	Osmotic coefficient (filtration efficiency), -

$\mu_{(\pm)}$	Chemical potential of cations and anions, J
$\tilde{\mu}_{(\pm)}$	Electrochemical potential of cations and anions, J
μ_w	Chemical potential of water, J
μ_f	Chemical potential of the salt, J
σ_S	Surface conductivity, S m^{-1}
σ_w	Conductivity of the pore water, S m^{-1}
$\sigma_{(\pm)}$	Contribution to the conductivity of the material, S m^{-1}
σ	Electrical conductivity of the porous material, S m^{-1}
ψ	Electrical potential due to the electrical double layer, V
φ	Electrical potential in the reservoir, V
$\tilde{\varphi}$	Electrical potential in the pore water, V
ρ_s	Mass density of the solid, kg m^{-3}
ρ_w	Mass density of the pore water, kg m^{-3}
π	Osmotic pressure in the reservoirs, Pa
$\tilde{\pi}$	Osmotic pressure in the pore space, Pa
$\delta\pi$	Difference in osmotic pressure between the reservoir and the pore water, Pa
η_w	Dynamic viscosity of the pore water phase, Pa s
Ω_w	Molecular volume of water, m^3
$\Omega_{(\pm)}$	Molecular volume of the anions and cations, m^3
Θ	Dimensionless variable, -
Θ_S	Value of Θ at saturation, -
ν	Dimensionless variable, -

Leroy et al., 2012). By unsaturated conditions, I consider that the pressure of the air phase is constant and therefore the mechanical driving force for the flow of the pore water is the gradient of the water pressure alone.

My goal is to apply the model developed in Paper 1 to study the filtration properties of charged porous materials such as bentonite in unsaturated conditions. This model is easily testable since all the conductivity and coupling terms of the matrix of material properties L are written in terms of the same fundamental parameters (permeability and cementation exponent) that can be measured independently. This is in contrast with the phenomenological models found in the literature and based on non-equilibrium thermodynamics without a micro-macro description of the coupling properties (e.g., Mitchell, 1993; Sherwood and Craster, 2000 for the saturated case, Chen and Hicks, 2013, for the unsaturated one). In some mechanistic models, the Donnan approach (Donnan, 1911) is used to represent the concentrations in the pore space of the porous body (e.g., Katchalsky and Curran, 1965). However, there are criticisms in the use of this model in the case of thin electrical double layers (e.g., at high salinities). In addition, most of these models do not account for the partition between the Stern and diffuse layers. Other micro-macro models ignore for instance the current density and electrostatic effects (e.g., Loret et al., 2002; Chen and Hicks, 2013) or consider the pore water phase being neutral (Dormieux et al., 1995). These models cannot therefore pretend to represent accurately transport phenomena in clay-rich materials with an excess of charge present in the pore water phase.

The goal of the present paper is to test various aspects of the model developed in Paper 1 against a range of experimental data in the context of diffusion and filtration (reverse osmosis) of a simple 1:1 salt like NaCl or KCl. Thanks to its filtration properties, highly charged porous media like bentonite are indeed used as permeability barriers in the shallow subsurface for environmental purposes (e.g., Malusis et al., 2003; Kang and Shackelford, 2009, 2010, 2011; Bohnhoff and Shackelford, 2013; Zhang et al., 2014) and for the containment of radioactive wastes (e.g., Bonaparte et al., 2008; Gens, 2013). We use the theory developed in Paper 1 to obtain new expressions for the osmotic filtration coefficient

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