Ionised Media

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Summary

High specific surface soils, rocks, gels and biological tissues are often ionised porous media. A porous medium model including an electroneutrality condition has been shown to provide a suitable description of some of their salient features [6]. These include among others, their swelling propensity [7], the occurrence of streaming and diffusion potentials and electro-osmosis.

Introduction

While hydraulic permeability is a quantity highly correlated to the characteristic pore size of the porous medium, electro-osmotic permeability depends minimally on the pore size of the medium. Consequently electrical phenomena become dominant over hydraulic phenomena in high specific surface media, such as clays or biological tissues, . In other words, the impact of electrical potential gradients are often more dominant on the fluid flow than a pressure gradient. Hence, classical Biot theories [1],[2] do not apply. Recent developments in electro-chemo-mechanical mixture theory [3],[4], [5] offer a framework in which to analyse the coupling of ionic, electrical and volume flow in ionised media. These models typically consist of an ionised solid, a fluid, and charged solutes. Numerous studies indicate that experimental data of various materials are well described using this approach [6], [7],[8], [9],[10]. In the following, the governing equations for a compressible ionised medium are presented. The nonlinear set of equations is transformed into a weak formulation and solved using the finite element method.

Theory

In this section the governing equations, as derived by [5], are given in the special case of infinitesimal quadriphasic mechanics of compressible charged porous media. Specific constitutive material behavior is considered and corresponding relations for the osmotic pressure and electrical potential at equilibrium are given. Finally the governing equations are reduced for a 1-dimensional configuration and decoupled. We consider a porous solid saturated with a monovalent ionic solution. The current volume fraction of the solid is φ^s, the current volume fraction of the ionic solution is φ^f. The corresponding initial volume fractions are φ_0^s, φ_0^f. The solution is a molecular mixture of water (w), cations (+) and anions (-). The partial densities of water, cations and anions are in the current state ρ^w, ρ^+ and ρ^-, and the in the initial state ρ_0^w, ρ_0^+ and ρ_0^-. The unstrained volume change ζ^β of constituent $\beta = w, +, -$ is :

$$\zeta^\beta = \frac{\rho^\beta - \rho_0^\beta}{\rho_i^\beta} \tag{1}$$

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in which ρ_i^β is an intrinsic reference density such that $\sum_{\beta=w,+,-} \frac{\rho_0^\beta}{\rho_i^\beta} = \phi_0^f$.

Balance laws

The momentum balance, neglecting inertia, reads:

$$\vec{\nabla} \cdot \sigma = 0, \tag{2}$$

with σ the Cauchy stress tensor. Mass balance of constituent α requires:

$$\frac{\partial \zeta^\beta}{\partial t} + \vec{\nabla} \cdot \left(\vec{v}^{\beta s}\right) = 0, \tag{3}$$

with $\vec{v}^{\beta s}$ the unstrained volume flux of constituent β with respect to the solid. In this paper α denotes all constituents, i.e. electrically charged solid (s), water (w), cations (+) and anions (-); β, γ all constituents except the charged solid matrix. As the mixture is assumed to be fully saturated,the following relation for the saturation condition holds:

$$\alpha \vec{\nabla} \cdot \vec{v}^s + \frac{1}{M}\frac{\partial p}{\partial t} - \sum_{\beta=w,+,-} \frac{\partial \zeta^\beta}{\partial t} = 0, \tag{4}$$

in which $\vec{v}^s$ is the solid velocity, α and M are the Biot coefficients. Electroneutrality requires:

$$\sum_{\beta=w,+,-} F \frac{z^\beta}{\bar{V}^\beta}\frac{\partial \zeta^\beta}{\partial t} = 0, \tag{5}$$

with F, z^β and $\bar{V}^\beta$ Faraday's constant, the valence and molar volume of constituent β respectively.

Constitutive behavior

The fluxes obey a coupled form of Darcy's, Fick's and Ohm's law:

$$\vec{v}^{\beta s} = - \sum_{\gamma=w,+,-} K^{\beta\gamma}\vec{\nabla}\mu^\gamma \quad \text{for} \quad \beta = w,+,-, \tag{6}$$

with $K^{\beta\gamma}$ a positive definite symmetric permeability matrix. In relationship (6) the electrochemical potentials, μ^β are defined as:

$$\mu^\gamma = \frac{\partial W}{\partial \zeta^\beta} + \frac{Fz^\beta}{\bar{V}^\beta}\xi, \tag{7}$$

with ξ and W the electrical potential and the energy function respectively.
The stress appearing in the momentum balance (2) is the partial derivative of the energy function W with respect to the infinitesimal strain tensor $\varepsilon = 1/2(\vec{\nabla}\vec{u} + (\vec{\nabla}\vec{u})^T)$, with $\vec{u}$ the displacement vector of the solid :

$$\sigma = \frac{\partial W}{\partial \varepsilon} \tag{8}$$

The pore pressure is given by the partial derivative of the same energy function W with respect to the difference between the strained porosity change $\varphi^f - \varphi_0^f$ and the unstrained volume change of the porosity $\sum_{\beta=w,+,-} \zeta^\beta$

$$p = -\frac{\partial W}{\partial(\varphi^f - \varphi_0^f - \sum_{\beta=w,+,-}\zeta^\beta)} \tag{9}$$

The energy function is the sum of the poroelastic strain energy and a mixing energy:

$$
\begin{aligned}
W = & -\alpha M tr\varepsilon \sum_{\beta=w,+,-}\zeta^\beta + \frac{1}{2}M(\sum_{\beta=w,+,-}\zeta^\beta)^2 + \frac{1}{2}(\frac{2\nu G}{1-2\nu} + \alpha^2 M)tr^2\varepsilon \\
& + G\varepsilon:\varepsilon + \frac{K_f}{2\varphi_0^f}(\varphi^f - \varphi_0^f - \sum_{\beta=w,+,-}\zeta^\beta)^2 + \sum_{\beta=w,+,-}\mu_0^\beta\zeta^\beta \\
& - RT\Gamma(\frac{\zeta^+}{\overline{V}^+} + \frac{\zeta^-}{\overline{V}^-})ln\zeta^w + RT\frac{\zeta^+}{\overline{V}^+}(ln\frac{\zeta^+}{\overline{V}^+}-1) + RT\frac{\zeta^-}{\overline{V}^-}(ln\frac{\zeta^-}{\overline{V}^-}-1)
\end{aligned}
\tag{10}
$$

The form (10) of W assumes linear isotropic elasticity and Donnan osmosis as the swelling mechanism of the shale. G is the shear modulus, ν is Poisson's ratio, K_f is the volumetric modulus of the solution, μ_0^β is the reference potential of constituent β, R is gas constant, T the absolute temperature and Γ the osmotic coefficient. Given this expression for the energy function, the electrochemical potentials (7) take the form:

$$\mu^w = \mu_0^w + p - RT\Gamma(\frac{\zeta^+}{\overline{V}^+\zeta^w} + \frac{\zeta^-}{\overline{V}^-\zeta^w}) \tag{11}$$

$$\mu^+ = \mu_0^+ + p + \frac{RT}{\overline{V}^+}ln\frac{\zeta^+}{(\zeta^w)^\Gamma} + \frac{F}{\overline{V}^+}\xi, \tag{12}$$

$$\mu^- = \mu_0^- + p + \frac{RT}{\overline{V}^-}ln\frac{\zeta^-}{(\zeta^w)^\Gamma} - \frac{F}{\overline{V}^+}\xi, \tag{13}$$

considering that

$$p = -K_f\frac{\varphi^f - \varphi_0^f - \sum_{\beta=w,+,-}\zeta^\beta}{\varphi_0^f} = -\alpha M tr\varepsilon + M\sum_{\beta=w,+,-}\zeta^\beta \tag{14}$$

The differential form of eqs. (11-13) is:

$$\frac{\partial}{\partial t}(\mu^\beta - \frac{Fz^\beta}{\overline{V}^\beta}\xi - p) = \sum_{\gamma=w,+,-}W^{\beta\gamma}\frac{\partial\zeta^\gamma}{\partial t}, \quad \beta = w,+,- \tag{15}$$

in which

$$W^{\beta\gamma} = \partial^2 W/\partial\zeta^\beta\partial\zeta^\gamma \tag{16}$$

The numerical implementation of the above equations is done along the lines of [11]. The displacements, the pressures, the electrochemical potentials of water, cations and anions, and the electrical potentials are the degrees of freedom.

$$
\begin{bmatrix}
\underline{S} & -\underline{L} & \underline{0} & \underline{0} \\
-\underline{L}^T & -\sum_{\beta,\gamma}\underline{C}_{\beta\gamma}-\dfrac{1}{M} & \sum_{\beta}\underline{C}_{\beta\gamma} & -\sum_{\beta,\gamma}\underline{C}_{\beta\gamma}\dfrac{z^{\beta}F}{\overline{V}^{\beta}} \\
\underline{0} & \sum_{\gamma}\underline{C}_{\beta\gamma} & -\underline{K}_{\beta\gamma}-\underline{C}_{\beta\gamma} & \sum_{\gamma}\underline{C}_{\beta\gamma}\dfrac{z^{\gamma}F}{\overline{V}^{\gamma}} \\
\underline{0} & -\sum_{\beta,\gamma}\underline{C}_{\beta\gamma}\dfrac{z^{\beta}F}{\overline{V}^{\beta}} & \sum_{\beta}\underline{C}_{\beta\gamma}\dfrac{z^{\beta}F}{\overline{V}^{\beta}} & -\sum_{\beta,\gamma}\dfrac{z^{\beta}F}{\overline{V}^{\beta}}\underline{C}_{\beta\gamma}\dfrac{z^{\gamma}F}{\overline{V}^{\gamma}}
\end{bmatrix}
\begin{bmatrix}
\delta\underline{u} \\
\delta\underline{p} \\
\delta\underline{\mu}^{\gamma} \\
\delta\underline{\xi}
\end{bmatrix}
=
\begin{bmatrix}
-\underline{R} \\
\underline{U}-\sum_{\beta}\underline{Q}_{\beta} \\
\underline{Q}_{\beta}+\sum_{\gamma}(\underline{T}_1+\underline{T}_2) \\
-\sum_{\alpha}\dfrac{z^{\beta}F}{\overline{V}^{\beta}}\underline{Q}_{\alpha}
\end{bmatrix}
$$

$$\underline{S}=\int_{\Omega}[(\vec{\nabla}\Phi\vec{e})^C:\frac{\partial^2 W}{\partial\epsilon^2}:\vec{\nabla}\Phi\vec{e}]\,d\Omega \qquad \underline{L}=\int_{\Omega}\alpha\vec{\nabla}\cdot\Phi\vec{e}p\,d\Omega$$

$$\underline{C}_{\alpha\beta}=\int_{\Omega}\underline{\Psi}(W^{\alpha\beta})^{-1}\underline{\Psi}^T\,d\Omega \qquad \underline{K}_{\alpha\beta}=\theta\int_{\Omega}\vec{\nabla}\underline{\Psi}^C\cdot K_{\alpha\beta}^*\cdot\vec{\nabla}\underline{\Psi}\Delta t\,d\Omega$$

$$\underline{R}=-\int_{\Gamma}\Phi\vec{e}\cdot\sigma\cdot\vec{n}\,d\Gamma-\int_{\Omega}\sigma_e\cdot\vec{\nabla}\Phi^I\vec{e}\,d\Omega+\int_{\Omega}\vec{\nabla}\cdot\Phi\vec{e}p\,d\Omega \qquad \underline{U}=\int_{\Omega}\underline{\Psi}(tr\epsilon-tr\epsilon_n+\frac{p-p_n}{M})\,d\Omega \qquad (17)$$

$$\underline{T}_1=\theta\int_{\Omega}(K_{\alpha\beta}\cdot\vec{\nabla}\mu^{\alpha})\cdot\vec{\nabla}\underline{\Psi}\Delta t\,d\Omega \qquad \underline{T}_2=(1-\theta)\int_{\Omega}(K_{\alpha\beta}\cdot\vec{\nabla}\mu_n^{\alpha})\cdot\vec{\nabla}\underline{\Psi}\Delta t\,d\Omega$$

$$\underline{Q}_{\beta}=\int_{\Omega}\underline{\Psi}(\zeta^{\beta}-\zeta_n^{\beta})\,d\Omega$$

Continuity of the displacements and the electrochemical potentials is enforced both within the elements as between element. As the displacement are continuous, but non-differentiable across the element interfaces, the strains, unstrained volumes and concentrations are discontinuous across the element boundaries. From eqs. 11, 12 and 13, one infers that the continuity of the electrochemical potentials is incompatible with the continuity of pressure and electrical potential, if the unstrained volumes are discontinuous. Hence, it is necessary not to enforce continuity of the pressure and the electrical potential.

Acknowledgement

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