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Analytical Solution of Compression, Free Swelling and Electrical Loading of Saturated Charged Porous Media

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Abstract. Analytical solutions are derived for one-dimensional consolidation, free swelling and electrical loading of a saturated charged porous medium. The governing equations describe infinitesimal deformations of linear elastic isotropic charged porous media saturated with a mono-valent ionic solution. From the governing equations a coupled diffusion equation in state space notation is derived for the electro-chemical potentials, which is decoupled introducing a set of normal parameters, being a linear combination of the eigenvectors of the diffusivity matrix. The magnitude of the eigenvalues of the diffusivity matrix correspond to the time scales for Darcy flow, diffusion of ionic constituents and diffusion of electrical potential.

Key words: osmosis, biological tissue, cartilage, clay, shale.

Nomenclature

α	s, f, +, -.
β, γ	f, +, -.
i	+, -.
\mathbf{A}	diffusivity matrix electro-chemical potentials.
\mathbf{E}_s	Green strain tensor of the solid.
\mathbf{B}	friction tensor.
\mathbf{D}_i^0	diffusion tensor ion i in free solution.
κ	permeability tensor.
\mathbf{u}	displacement vector solid.
$\mathbf{v}^{\beta s}$	velocity vector difference constituent β and the solid.
μ^β	electro-chemical potential constituent β .
p	pressure.
ξ	electrical potential.
n^α	volume fraction constituent α .
λ_i	eigenvalue corresponding to η_i .
\bar{V}^β	molar volume constituent β .
F	Faraday's constant.
R	universal gas constant.
T	temperature.

Γ	osmotic coefficient.
z^β	valence constituent β .
r	apparent hindrance factor.
G	shear modulus.
ν	Poisson's ratio.
ϵ	capacity.

1. Introduction

Shales, clays, gels and biological tissues exhibit swelling and shrinkage behavior induced by changes in external salt concentration Lai *et al.* (1991), Huyghe and Janssen (1997). Swelling and shrinkage results from the interaction between the fixed charges on the solid and ions present in the fluid resulting in Donnan-osmosis, electro-osmosis, streaming potentials and streaming currents, Mitchell (1993), Sachs and Grodzinsky (1987). In biological applications swelling is observed for cartilage, glycocalyx, cell and skin behavior. Swelling of shales is of major concern for petroleum engineering during active drilling, Heidug and Wong (1996), Oort (1997).

Lai *et al.* (1991) derived a small deformation triphasic formulation for soft charged hydrated tissues, considering all constituents incompressible. Huyghe and Janssen (1997) extended the chemo-electro-mechanical model to finite deformation behavior of a porous medium consisting of an electrically charged solid, liquid, cations and anions. This model has been implemented in a finite element formulation and is verified experimentally on one-dimensional transient behavior of annulus fibrosus tissue by Frijns *et al.* (1997). Similar numerical work has been done by Sun *et al.* (1999). Molenaar *et al.* (1998) recasted Frijns *et al.* (1997) model by including compressibility, an important feature of shales.

The verification of these models should be done on two levels. First one should address the question: does the numerical model solve the equations it claims to solve? Second, one should address the question: does the equations of electrochemomechanical theory describe the relationship between deformation, composition, mechanical load and external salt concentration in the material of interest correctly or not? The second question definitely requires experiments. But it also requires a reliable numerical solution procedure. Which requires to answer the first question first. The present paper addresses the first question not the second. In order to validate a numerical code to solve a set of partial differential equations analytical solutions are the only bench mark as is done for finite elasticity, Green and Zerna (1968) viscoelasticity, Laso and Öttinger (1993) and biphasic theory, Terzaghi (1923). The purpose of this paper is to fill this gap for electrochemomechanical theories and provide analytical solutions for transient conditions in addition to the simple equilibrium analytical solutions.

The governing equations of incompressible quadriphasic mechanics are presented shortly for the case of infinitesimal deformation of a mixture. For a one-dimensional situation these equations are decoupled giving a set of uncoupled diffusion

equations. Analytical solutions are presented for consolidation, free swelling and electrical loading under conditions of near electro neutrality, small deformations and concentration variations.

2. Theory

In this section the governing equations, as derived by Huyghe and Janssen (1997), are given in the special case of infinitesimal quadriphasic mechanics of incompressible charged porous media. Firstly the contribution of ions in the saturation condition is neglected, Section 2.1, consistent with Huyghe and Janssen (1997) whereafter they are incorporated, Section 2.2. 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 one-dimensional configuration and decoupled.

2.1. GOVERNING AND BALANCE EQUATIONS

Proceeding from Huyghe and Janssen (1997) the momentum balance, neglecting inertia and considering linear elastic solid behavior, reads

$$2G\nabla \cdot \mathbf{E}_s + \frac{2G\nu}{(1-2\nu)}\nabla \text{tr} \mathbf{E}_s - \nabla p = 0, \quad (1)$$

with G , ν , p and \mathbf{E}_s the shear modulus, Poisson ratio, pore pressure and strain tensor of the solid. The last is defined, under infinitesimal deformation, as $\mathbf{E}_s = 1/2(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)$, with \mathbf{u} the displacement vector of the solid. Mass balance of constituent α equals

$$\frac{\partial n^\alpha}{\partial t} + \nabla \cdot (n^\alpha \mathbf{v}^{\alpha s}) = 0, \quad (2)$$

with n^α the volume fraction of constituent α and $\mathbf{v}^{\alpha s}$ the velocity of constituent α with respect to the solid. In this paper α denotes all constituents, that is electrically charged solid (s), fluid (f), cations (+) and anions (-); β, γ all constituents except the charged solid matrix; i only ionic constituents. The mixture is assumed to be fully saturated giving the following relation for the saturation condition, neglecting the contribution of ionic constituents

$$\nabla \cdot \mathbf{v}^s + \nabla \cdot (n^f \mathbf{v}^{fs}) = 0. \quad (3)$$

Contrary to Huyghe and Janssen (1997) a small departure from electro-neutrality is considered for mathematical reasons as discussed later.

This results in the following analogy of Gauss' law, Lorrain *et al.* (1987):

$$\frac{\partial}{\partial t} \sum_{\beta=f,+,-} F \frac{z^\beta n^\beta}{\bar{V}^\beta} = \epsilon \frac{\partial \xi}{\partial t}, \quad (4)$$

with F , ξ , ϵ , z^β and \bar{V}^β Faraday's constant, electrical potential, capacity, the valence and molar volume of constituent β respectively. Temporary storage may be related to polarization of ions, water molecules and hydroxyl groups of proteoglycan fibers in human tissues or those on the surface of montmorillonites or shales, Lorrain *et al.* (1987), Karaborni *et al.* (1996). If relationships

$$-n^\beta \nabla \mu^\beta = \sum_{\gamma=f,+,-} \mathbf{B}^{\beta\gamma} \cdot \mathbf{v}^{\gamma s} \quad \text{for } \beta = f, +, -, \quad (5)$$

are fulfilled, with $\mathbf{B}^{\beta\gamma}$ positive definite symmetric friction matrices, the second law of thermodynamics is complied. In relationship (5) the electro-chemical potentials, μ^β are defined as

$$\mu^f = \frac{\partial W}{\partial n^f} + \frac{Fz^f}{\bar{V}^f} \xi + p, \quad (6)$$

$$\mu^i = \frac{\partial W}{\partial n^i} + \frac{Fz^i}{\bar{V}^i} \xi \quad \text{for } i = +, -, \quad (7)$$

with W the strain energy function.

2.2. INCORPORATION IONS IN THE SATURATION CONDITION

If the volume fraction of the cations and anions are not neglected we find contrary to (3)

$$\nabla \cdot \mathbf{v}^s + \sum_{\beta} \nabla \cdot (n^\beta \mathbf{v}^{\beta s}) = 0, \quad (8)$$

and instead of (7), Huyghe and Janssen (1997)

$$\mu^i = \frac{\partial W}{\partial n^i} + \frac{Fz^i}{\bar{V}^i} \xi + p \quad \text{for } i = +, -. \quad (9)$$

In principle, the pressure is always part of the electrochemical potential Katchalsky and Curran (1965). The relative importance of the pressure in the chemical potential is characterized by the ratio $p^* \bar{V} / RT \ln c / c_{\text{ref}}$ with p^* and c^* the characteristic pressure and molar concentration respectively. For dilute solutions at atmospheric pressure $p^* \bar{V} / RT \ln c / c_{\text{ref}}$ is small and consequently the contribution of the pressure to the electro-chemical potential of the ionic constituents can be neglected. With increasing pressure, that is at high depths during oil drilling, this is no longer justified. Under transient conditions the associated time scale of the individual contributions in conjunction with their relative magnitude to μ^i need to be considered.

2.3. CONSTITUTIVE BEHAVIOR

To focus the attention and without loss of generality, the strain energy function, W , is postulated to equal

$$\begin{aligned}
W(\mathbf{E}_s, n^\beta) = & \mu_0^f n^f + \mu_0^+ n^+ + \mu_0^- n^- - RT\Gamma \left(\frac{n^+}{\bar{V}^+} + \frac{n^-}{\bar{V}^-} \right) \ln n^f + \\
& + RT \frac{n^+}{\bar{V}^+} \left(\ln \frac{n^+ \bar{V}^+}{\bar{V}^+ n_{\text{ref}}^+} - 1 \right) + RT \frac{n^-}{\bar{V}^-} \left(\ln \frac{n^- \bar{V}^-}{\bar{V}^- n_{\text{ref}}^-} - 1 \right) + \\
& + \frac{G}{(1-2\nu)} \text{tr} \mathbf{E}_s \text{tr} \mathbf{E}_s + 2G \mathbf{E}_s : \mathbf{E}_s,
\end{aligned} \tag{10}$$

with Γ the osmotic coefficient. Expression (10) assumes linear isotropic elasticity and Donnan-osmosis as the driving force for swelling. Differentiating Equations (6) and (7) to time, rearranging and using the hypothesized relation for the strain energy function, $W = W(\mathbf{E}_s, n^\beta)$ gives

$$\frac{\partial}{\partial t} \left(\mu^f - \frac{Fz^f}{\bar{V}^f} \xi - p \right) = \sum_{\gamma=f,+,-} \mathbf{W}^{f\gamma} \frac{\partial n^\gamma}{\partial t}, \tag{11}$$

$$\frac{\partial}{\partial t} \left(\mu^i - \frac{Fz^i}{\bar{V}^i} \xi \right) = \sum_{\gamma=f,+,-} \mathbf{W}^{i\gamma} \frac{\partial n^\gamma}{\partial t} \quad \text{for } i = +, - \tag{12}$$

with $\mathbf{W}^{\beta\gamma} = \partial^2 W / \partial n^\beta \partial n^\gamma$ and use is made of the observation that $\partial^2 W / \partial \mathbf{E}_s \partial n^\alpha = 0$. The components of the friction matrix are related to diffusion coefficients of fluid and ions as derived by Molenaar *et al.* (1999)

$$\mathbf{B}^{\text{ff}} = n_f^2 \mathbf{K}^{-1} - (1-r) \mathbf{B}^{\text{f}^+} - (1-r) \mathbf{B}^{\text{f}^-}, \tag{13}$$

$$\mathbf{B}^{ii} = -\frac{\mathbf{B}^{if}}{1-r}, \tag{14}$$

$$\mathbf{B}^{if} = -n^f RT c^i \mathbf{D}_i^{0-1}, \tag{15}$$

$$\mathbf{B}^{+-} = 0, \tag{16}$$

with R the universal gas constant, r the hindrance factor, T the absolute temperature, \mathbf{K} the permeability tensor, \mathbf{D}_i^0 the ion diffusion tensor in free water and c^i the concentration. Contrary to Mow *et al.* (1998) and Lai *et al.* (2000) the components \mathbf{B}^{if} are unequal to zero.

2.4. EQUILIBRIUM RELATIONSHIPS

Finally relations are given valid at equilibrium. At Donnan-equilibrium the internal and external electro-chemical potentials of the fluid and ions are equal, $\mu_i^\beta = \mu_c^\beta$. This gives for the osmotic pressure, Huyghe and Janssen (1997)

$$p = RT (\Gamma(c_i^+ + c_i^-) - (c_e^+ + c_e^-)). \tag{17}$$

The electrical potential difference between the external solution and the porous medium is given by the Nernst potential

$$\xi = \frac{RT}{F} \ln \left(\frac{c_e^+}{c_i^+} \right). \tag{18}$$

Fulfilling electro neutrality at equilibrium the following relations for internal ionic concentrations and volume fractions are obtained, Huyghe and Janssen (1997)

$$c_i^+ = \frac{1}{2} \left(-c^{fc} + \sqrt{c^{fc2} + 4c_e^{+2}} \right), \quad (19)$$

$$c_i^- = \frac{1}{2} \left(+c^{fc} + \sqrt{c^{fc2} + 4c_e^{-2}} \right), \quad (20)$$

$$n^+ = n^f \bar{V}^+ c_i^+, \quad n^- = n^f \bar{V}^- c_i^-, \quad (21)$$

with c^{fc} the fixed charge concentration.

2.5. REDUCTION TO ONE-DIMENSIONAL CONFIGURATION

The general constitutive relations presented above are simplified for a one-dimensional situation assuming constant material parameters, small deformations and concentration variations. Momentum balance (1) reduce to

$$H \frac{\partial^2 u}{\partial x^2} - \frac{\partial p}{\partial x} = 0, \quad (22)$$

with $H = 2(1 - \nu)G/(1 - 2\nu)$ the one-dimensional bulk modulus. Following Terzaghi (1923) the momentum balance equation is integrated with respect to the x -coordinate yielding:

$$H \frac{\partial u}{\partial x} - p = f(t), \quad (23)$$

differentiated with respect to time giving

$$H \frac{\partial^2 u}{\partial x \partial t} - \frac{\partial p}{\partial t} = \frac{\partial f(t)}{\partial t}. \quad (24)$$

In the two preceding equations $f(t)$ is the external load on the sample. For consolidation an instantaneous mechanical loading at $t = t_0$ is considered and the external mechanical loading remains unaltered for free swelling. Therefore in both cases the right-hand side of Equation (24) equals zero for $t > t_0$. Substitution of the obtained Equation (24) into the reduced saturation condition in order to eliminate the displacement yields

$$\frac{1}{H} \frac{\partial p}{\partial t} - \frac{\partial n^f}{\partial t} = 0. \quad (25)$$

Manipulation of Equation (5) and substitution into the mass balance of constituents β results in

$$\frac{\partial n^\beta}{\partial t} - \sum_{\gamma=f,+, -} \mathbf{P}^{\beta\gamma} \frac{\partial \mu^\gamma}{\partial x^2} = 0 \quad \text{for } \beta = f, +, -, \quad (26)$$

with the matrix \mathbf{P} equal to $\mathbf{P}^{\beta\gamma} = n^\beta n^\gamma (\mathbf{B}^{-1})^{\beta\gamma}$. The preceding equation assumes \mathbf{P} constant considering spatial volume fraction variations to be sufficiently small. Substitution of Equations (11) and (12) into Equations (25), (4) and (26) gives

$$\left(\frac{1}{H} + \mathbf{C}^{\text{ff}}\right) \frac{\partial p}{\partial t} - \sum_{\beta=\text{f},+,-} \mathbf{C}^{\text{f}\beta} \frac{\partial}{\partial t} \left(\mu^\beta - \frac{F z^\beta}{\bar{V}^\beta} \xi \right) = 0, \quad (27)$$

$$\sum_{\beta=\text{f},+,-} F \frac{z^\beta}{\bar{V}^\beta} \left[\sum_{\gamma=\text{f},+,-} \mathbf{C}^{\beta\gamma} \frac{\partial}{\partial t} \left(\mu^\gamma - \frac{F z^\gamma}{\bar{V}^\gamma} \xi \right) - \mathbf{C}^{\beta\text{f}} \frac{\partial p}{\partial t} \right] = \epsilon \frac{\partial \xi}{\partial t}, \quad (28)$$

$$\sum_{\gamma=\text{f},+,-} \left[\mathbf{C}^{\beta\gamma} \frac{\partial}{\partial t} \left(\mu^\gamma - \frac{F z^\gamma}{\bar{V}^\gamma} \xi \right) - \mathbf{P}^{\beta\gamma} \frac{\partial^2 \mu^\gamma}{\partial x^2} \right] - \mathbf{C}^{\beta\text{f}} \frac{\partial p}{\partial t} = 0$$

for $\beta = \text{f}, +, -, \quad (29)$

with $\mathbf{C} = \mathbf{W}^{-1}$. Equations (27) and (28) are rewritten in state-space notation commonly used in dynamics and control engineering giving, Slotine and Li (1991)

$$\mathbf{Z} \frac{\partial}{\partial t} [p \ \xi]^T = \mathbf{Q} \frac{\partial}{\partial t} [\mu^{\text{f}} \ \mu^+ \ \mu^-]^T, \quad (30)$$

with

$$\mathbf{Z} = \begin{bmatrix} 1/H + \mathbf{C}^{\text{ff}} & \sum_{\beta} \mathbf{C}^{\text{f}\beta} \frac{F z^\beta}{\bar{V}^\beta} \\ \sum_{\beta} F \frac{z^\beta}{\bar{V}^\beta} \mathbf{C}^{\beta\text{f}} & \sum_{\beta} \sum_{\gamma} \mathbf{C}^{\beta\gamma} \frac{F^2 z^\beta z^\gamma}{\bar{V}^\beta \bar{V}^\gamma} + \epsilon \end{bmatrix}, \quad (31)$$

$$\mathbf{Q} = \begin{bmatrix} \mathbf{C}^{\text{ff}} & \mathbf{C}^{\text{f}+} & \mathbf{C}^{\text{f}-} \\ \sum_{\beta} F \frac{z^\beta}{\bar{V}^\beta} \mathbf{C}^{\beta\text{f}} & \sum_{\beta} F \frac{z^\beta}{\bar{V}^\beta} \mathbf{C}^{\beta+} & \sum_{\beta} F \frac{z^\beta}{\bar{V}^\beta} \mathbf{C}^{\beta-} \end{bmatrix}. \quad (32)$$

Substitution of Equation (30) into (29) gives

$$\frac{\partial}{\partial t} [\mu^{\text{f}} \ \mu^+ \ \mu^-]^T = \mathbf{A} \frac{\partial^2}{\partial x^2} [\mu^{\text{f}} \ \mu^+ \ \mu^-]^T \quad (33)$$

with

$$\mathbf{A} = \mathbf{E}^{-1} \cdot \mathbf{P}, \quad (34)$$

$$\mathbf{E} = \mathbf{C} - \mathbf{Q}^T \cdot \mathbf{Z} \cdot \mathbf{Q}. \quad (35)$$

This coupled set of equations can be decoupled using the matrix identity

$$\mathbf{A} = \mathbf{M} \cdot \mathbf{\Lambda} \cdot \mathbf{M}^{-1}. \quad (36)$$

The diagonal matrix \mathbf{A} has the eigenvalues of \mathbf{A} on the diagonal elements and \mathbf{M} the corresponding eigenvectors, Slotine and Li (1991). A set of normal parameters is introduced, resulting in three uncoupled diffusion equations

$$\frac{\partial \eta_i}{\partial t} = \lambda_i \frac{\partial^2 \eta_i}{\partial x^2} \quad \text{for } i = 1, 2, 3 \quad (37)$$

with,

$$\begin{bmatrix} \eta_1 & \eta_2 & \eta_3 \end{bmatrix}^T = \mathbf{M}^{-1} \begin{bmatrix} \mu^f & \mu^+ & \mu^- \end{bmatrix}^T. \quad (38)$$

The derivation for the case where the contribution of the volume fractions of the ions is incorporated into the saturation condition is along the same line as presented above. Solutions of the diffusion equation are thoroughly treated in for example Carslaw and Jaeger (1957).

3. Consolidation, Free Swelling and Electrical Loading

In this section solutions are given for consolidation, free swelling and electrical loading of a porous medium with respect to an initial steady reference state at $t = t_0$ assuming constant material parameters and small deformations. A homogeneous sample is considered placed frictionless in a holder. At the bottom, $x = 0$, the sample is in contact with a glass filter saturated by a sodium chloride solution. An impermeable piston is placed on top of the sample, $x = L$, where an external mechanical load is applied. The following mixture parameters and initial conditions are considered and capacity is chosen small, $\epsilon = 10^{-24} \text{ C}^2/\text{Nm}^4$, Weast (1976)

$$\begin{aligned} H &= 2 \times 10^2 \text{ MPa}, & c^{fc} &= -0.2 \text{ moleq/l}, & \Gamma &= 0.9 [-], \\ D_0^+ &= 13.3 \times 10^{-10} \text{ m}^2/\text{s}, & c_e^+ &= c_e^- = 1.0 \text{ mol/l}, & n^f &= 0.2, \\ D_0^- &= 20.3 \times 10^{-10} \text{ m}^2/\text{s}, & \bar{V}^+ &= 2.3 \times 10^{-6} \text{ m}^3/\text{mol}, & r &= 0.4, \\ \kappa &= 5.0 \times 10^{-17} \text{ m}^4/\text{Ns}, & \bar{V}^- &= 15.2 \times 10^{-6} \text{ m}^3/\text{mol}, & T &= 293 \text{ K}, \end{aligned}$$

typical for clays.

3.1. CONSOLIDATION

For consolidation a stepwise change of the load on the piston is applied at $t = t_0$ equal to $f(t) = -p_0 \mathcal{H}(t - t_0)$, with $\mathcal{H}(t - t_0)$ the Heaviside function. The magnitude of p_0 is assumed sufficiently small in order to ensure that \mathbf{W} and \mathbf{P} are constant in time. For consolidation the following initial and boundary conditions on the electro-chemical potentials, pressure, electrical potentials and displacement with respect to the steady reference state at $t = t_0$

$$\mu^f(0, t) = 0, \quad \partial \mu^f / \partial x(L, t) = 0, \quad \mu^f(x, t_0) = p_0,$$

$$\begin{aligned}
\mu^+(0, t) &= 0, & \partial\mu^+/\partial x(L, t) &= 0, & \mu^+(x, t_0) &= 0, \\
\mu^-(0, t) &= 0, & \partial\mu^-/\partial x(L, t) &= 0, & \mu^-(x, t_0) &= 0, \\
p(0, t) &= 0, & p(x, t_0) &= p_0, & \xi(x, t_0) &= 0, \\
u(0, t) &= 0, & u(x, t_0) &= 0, & \xi(0, t) &= 0.
\end{aligned} \tag{39}$$

Utilizing the method of separation of variables a relation for the electro-chemical potentials is obtained given by

$$\begin{bmatrix} \mu^f(x, t) \\ \mu^+(x, t) \\ \mu^-(x, t) \end{bmatrix} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin\left(\frac{2n+1}{2} \frac{\pi}{L} x\right) \mathbf{M} \cdot \mathbf{R}_n \cdot \mathbf{M}^{-1} \cdot \begin{bmatrix} p_0 \\ 0 \\ 0 \end{bmatrix}, \tag{40}$$

with \mathbf{R}_n a diagonal matrix with on its diagonal elements

$$\mathbf{R}_n^{ii} = \exp\left(\left(\frac{2n+1}{2}\pi\right)^2 \frac{\lambda^i(t-t_0)}{L^2}\right). \tag{41}$$

Using relation (30) and incorporation of the initial and boundary conditions on the pore pressure and electrical potential gives

$$\begin{bmatrix} p(x, t) \\ \xi(x, t) \end{bmatrix} = \mathbf{Z}^{-1} \cdot \mathbf{Q} \cdot \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin\left(\frac{2n+1}{2} \frac{\pi}{L} x\right) \times \\
\times \mathbf{M} \cdot (\mathbf{R}_n - \mathbf{I}) \cdot \mathbf{M}^{-1} \cdot \begin{bmatrix} p_0 \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} p_0 \\ 0 \end{bmatrix}. \tag{42}$$

Substitution of the obtained relation for the pressure in Equation (23), integrating with respect to x and incorporation of the boundary condition $u(0, t) = 0$ gives for the displacement

$$\begin{aligned}
u(x, t) &= \frac{1}{H} [1 \ 0] \cdot \mathbf{Z}^{-1} \cdot \mathbf{Q} \cdot \frac{8L}{\pi^2} \times \\
&\times \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \left(1 - \cos\left(\frac{2n+1}{2} \frac{\pi}{L} x\right)\right) \times \\
&\times \mathbf{M} \cdot (\mathbf{R}_n - \mathbf{I}) \cdot \mathbf{M}^{-1} \cdot \begin{bmatrix} p_0 \\ 0 \\ 0 \end{bmatrix}. \tag{43}
\end{aligned}$$

3.2. FREE SWELLING

A change in the external concentration is considered for free swelling of the sample. The electro-chemical potentials for the sodium chloride solution in the glass filter are equal to

$$\mu^f = -RT (c_e^+ + c_e^-), \quad \mu^i = \frac{RT}{\bar{V}^i} \ln \frac{c_e^i}{c_{\text{ref}}^i} + \frac{Fz^i}{\bar{V}^i} \xi, \quad (44)$$

with c_e^i the external concentrations. For free swelling the following set of boundary conditions is applied with respect to the initial steady state situation

$$\begin{aligned} \mu^f(0, t) &= -RT (\Delta c_e^+ + \Delta c_e^-), & \frac{\partial \mu^f}{\partial x}(L, t) &= 0, & \mu_f(x, t_0) &= 0, \\ \mu^+(0, t) &= \frac{RT}{\bar{V}^+} \ln \frac{c_e^+(t_0^+)}{c_e^+(t_0^-)}, & \frac{\partial \mu^+}{\partial x}(L, t) &= 0, & \mu^+(x, t_0) &= 0, \\ \mu^-(0, t) &= \frac{RT}{\bar{V}^-} \ln \frac{c_e^-(t_0^+)}{c_e^-(t_0^-)}, & \frac{\partial \mu^-}{\partial x}(L, t) &= 0, & \mu^-(x, t_0) &= 0, \\ p(0, t) &= 0, & p(x, t_0) &= 0, & \xi(x, t_0) &= 0, \\ u(0, t) &= 0, & u(x, t) &= 0, & \xi(0, t) &= 0, \end{aligned} \quad (45)$$

with Δc_e^+ , Δc_e^- the change in external concentration of cation and anion and t_0^- and t_0^+ time just before and after t_0 when chemical loading is applied. The change in the external concentration is considered sufficiently small such that firstly \mathbf{W} and \mathbf{P} are considered constant in time and secondly the change of the electro-chemical potentials of the ions is approximately linear. Introducing a new parameter as,

$$\zeta_i(x, t) = \eta_i(x, t) - \eta_i(0, t), \quad (46)$$

a set of homogeneous boundary conditions and inhomogeneous initial conditions similar to consolidation are obtained. The solution for the electro-chemical potentials, pore pressure, electrical potential and displacement are obtained analogous to consolidation as described in the preceding section.

3.3. ELECTRICAL LOADING

Electrical loading of charged saturated porous media can be used to characterize material parameters, Sachs and Grodzinsky (1987). A pure hypothetical situation is considered where the piston and holder are considered as perfect electrical insulators and an electrical potential is applied at the filter resulting in boundary conditions at $x = 0$ equal to

$$\xi(x, t) = \xi_0, \quad \mu^f(0, t) = 0, \quad \mu^i(0, t) = \frac{Fz^i}{\bar{V}^i} \xi_0, \quad (47)$$

with remaining initial and boundary conditions at $x = L$ given in Equation (45). As boundary conditions are identical to free swelling the solution obtained for free swelling can be applied directly.

In the case of incorporation of the ion volume fractions into the saturation condition only the boundary conditions for consolidation change as follows directly from Equation (9).

4. Results

4.1. NEGLECTING IONS IN THE SATURATION CONDITION

In this section results are presented for consolidation, free swelling and electrical loading for the material model where the contribution of the ions in the saturation condition is considered to be small. For the material parameters considered the three eigenvalues equal

$$\begin{aligned}\lambda_1 &= 1.04 \times 10^{-8} \text{ m}^2/\text{s}, & \lambda_2 &= 9.44 \times 10^{-10} \text{ m}^2/\text{s}, \\ \lambda_3 &= 1.58 \times 10^0 \text{ m}^2/\text{s}.\end{aligned}\quad (48)$$

First consolidation is considered where the external mechanical load is equal to $p_0 = 0.05$ MPa, with boundary conditions given by relation (39). The pore pressure at $x = L$, just below the impermeable piston, is presented in Figure 1. The time for consolidation to occur is approximately equal to $t - t_0 \approx 0.035$ h. The transient behavior of the displacement is self-similar as they are directly coupled by the momentum balance, such that the contribution of pore pressure and solid deformation balances the external load at all times.

In order to let the sample swell the external salt concentration is decreased with a small amount from $c_e^+ = c_e^- = 1.0$ mol/l to $c_e^+ = c_e^- = 0.995$ mol/l, with boundary

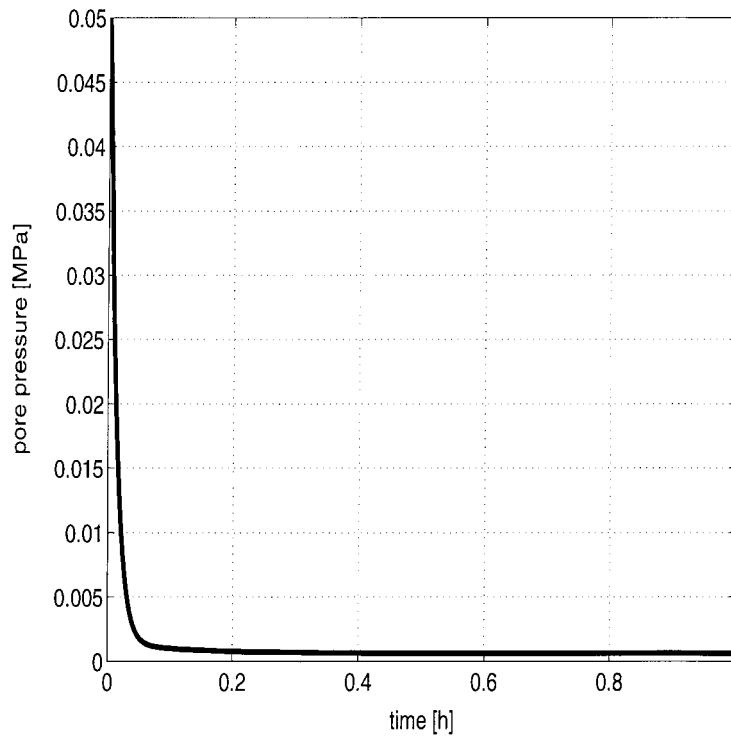


Figure 1. Pore pressure at $x = L$ for consolidation.

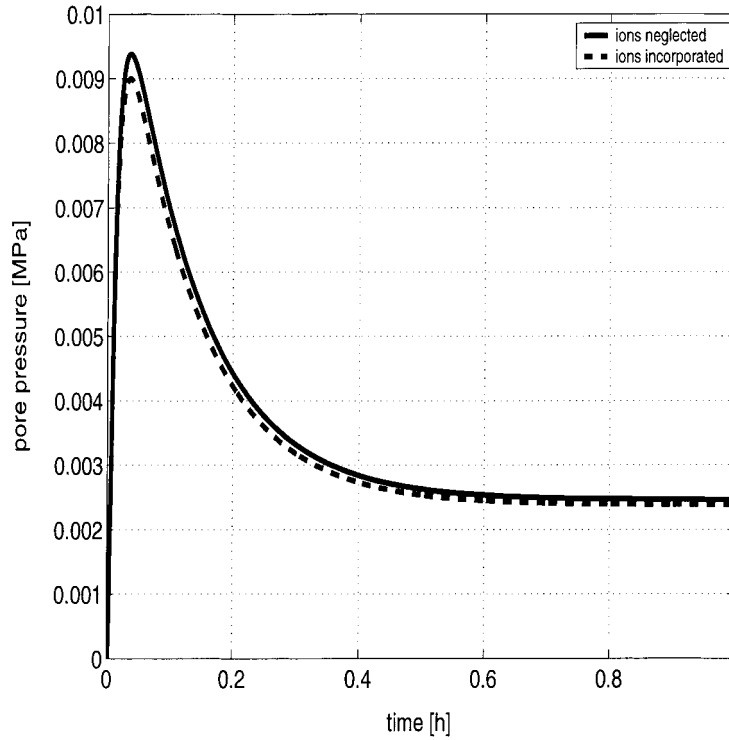


Figure 2. Pore pressure at $x = L$ during free swelling for neglecting (—) and incorporating (---) the ions in the saturation conditions.

condition given in relation (45). The pore pressure and displacement at $x = L$ are presented in Figures 2 and 3 respectively. The pore pressure increases fast reaching a maximum value at approximately $t - t_0 \approx 0.035$ h, whereafter the sample partly shrinks till an equilibrium is obtained after $t - t_0 \approx 0.6$ h. Changing the external concentration results in a fluid flux in and an ionic flux out of the sample. The overshoot of the pore pressure and corresponding displacement results from the faster fluid flow into compared to the flux of ionic constituents out of the sample. The osmotic pressure and electrical potential (not shown) at equilibrium are equal to the difference between the values obtained via relationship (17) and (18) respectively evaluated for the old and new external concentration, using relationships (19) and (20).

Finally an increase of the electrical potential equal to $\xi = \xi_0$ is applied at the filter with boundary conditions given by relations (45) and (47). For increasing magnitude of ϵ an approximately linear decrease of time scale is observed, corresponding to increasing temporarily polarization within the sample. The transient electrical potential response from $\xi = 0$ to $\xi = \xi_0$ is similar to that of an ordinary diffusion equation, characterized by the third eigenvalue, λ_3 , till the equilibrium value is reached of $\xi_0 = 0.01$ mV.

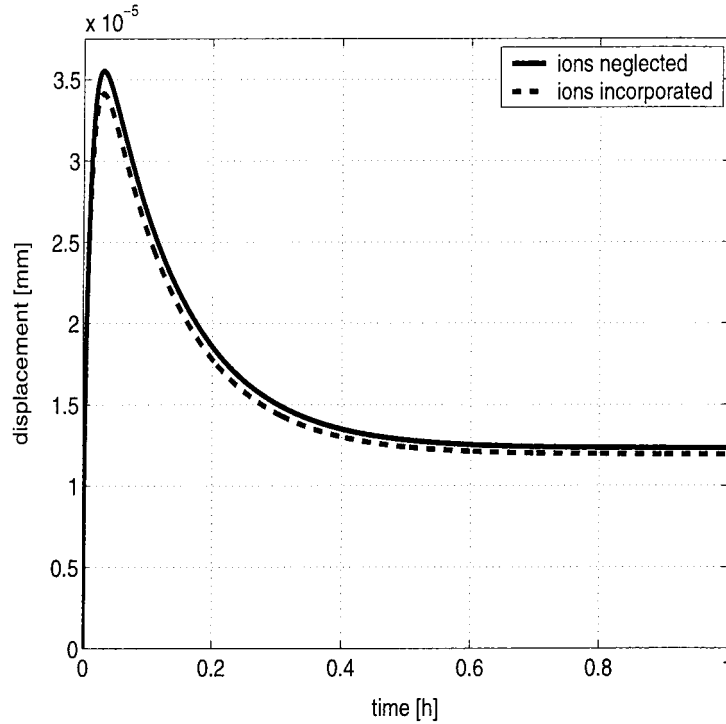


Figure 3. Displacement at $x = L$ during free swelling for neglecting (—) and incorporating (---) the ions in the saturation conditions.

4.2. INCORPORATION OF THE IONS IN THE SATURATION CONDITION

In this subsection the results are shown for the transient behavior of the pore pressure and displacement during free swelling if the volume fractions of the ions are incorporated into the saturation condition, Equation (8). Considering identical material parameters as above the eigenvalues equal

$$\begin{aligned}\lambda_1 &= 1.02 \times 10^{-8} \text{ m}^2/\text{s}, & \lambda_2 &= 9.33 \times 10^{-10} \text{ m}^2/\text{s}, \\ \lambda_3 &= 1.58 \times 10^0 \text{ m}^2/\text{s}.\end{aligned}\quad (49)$$

The magnitude of all three eigenvalues have changed only slightly, about 3% for the first and less than 1% for the second. The pore pressure and displacement are presented in Figures 2 and 3 respectively. The pore pressure increases fast reaching a maximum at $t \approx 0.035$ h whereafter the pore pressure reduces till an equilibrium state is reached. The maximum pore pressure has however reduced with about 5% compared to the previous case where the contribution of the ionic volume fractions is neglected. For increasing difference between λ_1 and λ_2 the difference in maximum pore pressure increases strongly. Furthermore the change in Donnan-pressure at equilibrium is slightly lower.

5. Discussion

Analytical solutions are presented for the electrochemomechanical theory as developed by Lai *et al.* (1991) and Huyghe and Janssen (1997). They can serve as benchmarks for the transient behavior of finite element codes developed for the theory. The solutions are however restricted to small deformation and concentration variations and have no practical application.

In Section 3 the analytical solutions are presented for consolidation, free swelling and electrical loading. These solutions are only applicable if the eigenvalues are positive, that is \mathbf{A} is positive definite. Otherwise finite perturbations in the external load or external salt concentration would result in infinite deformations. Although both \mathbf{W} and \mathbf{B} are required to be positive definite, Huyghe and Janssen (1997), it is not evident that these restrictions are sufficient to demonstrate positive definiteness of the matrix \mathbf{A} . Introduction of temporary storage of charge, by means of a dielectric constant is done to positively influence the stability of the matrix \mathbf{A} and has a small influence on the macroscopic behavior.

As shown in the preceding section the time corresponding to both the end of consolidation to and the maximum pore pressure development occurs at $t - t_0 \approx 0.035$ h. From this it may be concluded that the term λ_1/L^2 is closely related to the typical time scale for fluid flow. Further it is noted that the value of λ_1/L^2 corresponds to the typical time scale of fluid flow in a bi-phasic mixture which is equal to $\kappa H/L^2$. The second eigenvalue is related to the time scale corresponding to ionic mass transfer incorporating the hindrance factor r , $\lambda_2/L^2 \approx 2(1 - r)(1/D_0^+ + 1/D_0^-)/L^2$, Kemenade (1998). For the considered material parameter the magnitude of λ_2/L^2 gives a first *indication* for the time when equilibrium is reached for free swelling as the reduction of the ionic electro-chemical potentials is partly achieved by an increase of the fluid content. The third eigenvalue is associated with the diffusion of electrical potential and is strongly dependent on capacity, ϵ . In view of the observations made by Lai *et al.* (2000) it is noted that increasing the fixed charge concentration decreases both λ_1 and λ_2 .

If the contribution of the ions is not neglected a difference in the swelling behavior is observed even for dilute solutions, which increases for increasing difference in magnitude between λ_1 and λ_2 . The interpretation of the eigenvalues is identical as discussed above. The magnitude of the maximum pore pressure is observed to reduce with about 5% together with a slight change in Donnan-pressure. If electroneutrality holds, $\epsilon = 0$, only two time scales are present associated with fluid flow or pore pressure diffusion and diffusion of ionic constituents, describing the transient behavior of the mixture.

Solutions for axisymmetric configurations may be obtained under plain stress or strain conditions. For a more general configuration the route taken by Biot (1956) may be used. Application to compressible mixtures theories of Biot (1956), Molenaar *et al.* (1998) can be easily made.

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