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An Analytical Solution of Incompressible Charged Porous Media

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Abstract

A one-dimensional analytical solution is derived for free swelling and consolidation of a saturated charged porous medium. The derived equations describe infinitesimal deformation of charged porous media saturated with a fluid with dissolved cations and anions. In the one-dimensional case the governing equations reduce to a coupled diffusion equations for electro-chemical potentials. Suitable initial and boundary conditions based on consolidation or free swelling experiments complete the equations.

Keywords: mixture theory, porous media, biological tissues, analytical solutions

AMS subject classification: 76S05, 33C10, 35M10, 74B05, 74F10, 15A23

Notations

a	scalar
\mathbf{a}	vector
A	scalar
\mathbf{A}	matrix
\mathcal{A}	tensor

Nomenclature

c	molar concentration of the fluid phase	[mol m ⁻³]
c^β	molar concentration of ion β per unit fluid volume	[mol m ⁻³]
c^{fc}	molar concentration of fixed charge per unit fluid volume	[mol m ⁻³]
D^β	diffusivity of ion β	[m ² s ⁻¹]
F	Faraday's constant	[C mol ⁻¹]
K	hydraulic permeability	[m ⁴ N ⁻¹ s ⁻¹]
p	pressure of the fluid phase	[N m ⁻²]
r	apparent hindrance factor	[-]
R	universal gas constant	[J mol ⁻¹ K ⁻¹]
t	time	[s]
T	absolute temperature	[K]
\mathbf{U}	displacement	[m]
\bar{V}^β	partial molar volume of ion β	[m ³ mol ⁻¹]
z^β	valence of ion β	[-]
z^{fc}	valence of fixed charge	[-]
$\mathcal{E}(\mathbf{U})$	strain tensor	[-]
λ_s	Lamé stress constant	[N m ⁻²]
μ^f	electro-chemical potential of the fluid phase	[N m ⁻²]
μ^β	electro-chemical potential of ion β	[N m ⁻²]
μ_s	Lamé stress constant	[N m ⁻²]
ξ	voltage	[V]
φ^α	volume fraction of the α -phase	[-]
φ^β	volume fraction of ion β	[-]
Γ	osmotic coefficient of ion β	[-]

1 Introduction and Motivation

Cartilaginous tissues are soft hydrated tissues with strong swelling and shrinking properties. This swelling and shrinkage behaviour of cartilaginous tissues is caused by the flow of water that is bound to the charged solid skeleton of porous tissue. The driving mechanism is an interplay of mechanical, chemical and electrical forces. Swelling and shrinkage can be modelled by a four-component mixture theory [8, 3] in which the deformable and charged porous medium is saturated with a fluid with dissolved cations and anions.

The solid skeleton and fluid are assumed to be intrinsically incompressible and therefore a non-zero fluid flux divergence gives rise to swelling or shrinkage of the porous medium. Alternatively, a gradient in the fluid pressure, ion concentrations or voltage results in flow of the fluid and ions [3]. This model has been implemented in a finite element formulation [9, 3] and is verified experimentally [4].

In the earlier work [10], a set of analytical solutions has been derived to verify the finite element solution of model. However, in mass balances [10, equation 2], the time derivatives of volume fractions are considered instead of their material time derivatives. This can only be done if the Lagrangian coordinate is considered. Also the diagonalization [10, equation 36] produces complex eigenvalues, therefore the obtained solution series are no longer valid. In fact, the equations in this case are of hyperbolic type.

We set ourselves the task of resolving this problem. In this paper, all scalar and vectorial functions are defined in the Lagrangian coordinates as based on [14]. The reduced coupled system of diffusion equations are also diagonalized using the real positive eigenvalues.

This paper is outlined as follows. Section 2 sketches the physical model based on the concept of mixture theory. Section 3 considers the one-dimensional model following [13, 1] to derive a coupled system of diffusion equations. Section 4 is devoted to derive a set of solutions for two experiments, consolidation and free swelling. The solutions for these two experiments are displayed in section 5.

2 Governing equations

Within the concept of mixture theory, we consider a porous solid skeleton and an immiscible pore-fluid. The idea is to present the saturated porous medium as a superposition of deformable phases that occupy the same domain in the three-dimensional space at time t . In other words, we assume that different phases exist simultaneously at each point in space. Cartilaginous tissues are assumed to consist of two phases, a solid phase and a fluid phase. In cartilaginous tissues, the fluid phase consists of three constituents: liquid, cation and anion. We shall use the abbreviation s and f respectively for the solid and fluid phase. Also $+$ and $-$ are used for the cation and anion constituent.

Let's choose the configuration $\Omega_{t_0} \subset \mathbb{R}^3$ of the solid skeleton at an initial instant of time t_0 as the reference configuration for the Lagrangian description. The reference configuration need not be a stress-free configuration. In fact, the stress \mathcal{P}_0 is defined in the reference configuration and obeys the momentum balance

$$\text{Div } \mathcal{P}_0 = \mathbf{0}. \tag{2.1}$$

The motion of the skeleton is described by the following diffeomorphic mapping

$$\forall t \geq t_0 : \chi(\cdot, t) : \Omega_{t_0} \rightarrow \Omega_t \subset \mathbb{R}^3, \quad \Omega_t := \chi(\Omega_{t_0}, t), \quad (2.2)$$

where Ω_t denotes the actual configuration of the solid skeleton in the three-dimensional Euclidean configuration. The velocity and the deformation for the solid skeleton at the material point \mathbf{X} in the reference configuration Ω_{t_0} are defined by the relations

$$\dot{\mathbf{x}}^s = \frac{\partial \chi}{\partial t}(\mathbf{X}, t), \quad \mathcal{F} = \frac{\partial \chi}{\partial \mathbf{X}} \equiv \text{Grad} \chi(\mathbf{X}, t), \quad J = \det \mathcal{F} > 0, \quad (2.3)$$

by Grad, we mean the gradient operator in the reference configuration Ω_{t_0} . The Eulerian velocity \mathbf{v}^s of the solid skeleton is followed by the change of variables

$$\mathbf{v}^s = \dot{\mathbf{x}}^s(\chi^{-1}(\mathbf{x}, t), t) = \mathbf{v}^s(\mathbf{x}, t), \quad \mathbf{x} \in \Omega_t. \quad (2.4)$$

In the classical theory of mixtures the motion of β -th constituent, $\beta = f, +, -$, is described by the Eulerian velocity fields

$$\mathbf{v}^\beta = \mathbf{v}^\beta(\mathbf{x}, t), \quad \beta = f, +, -, \quad \mathbf{x} \in \Omega_t. \quad (2.5)$$

We transform these fields into the material description of the skeleton

$$\dot{\mathbf{x}}^\beta = \mathbf{v}^\beta(\chi(\mathbf{X}, t), t) = \dot{\mathbf{x}}^\beta(\mathbf{X}, t), \quad \beta = f, +, -. \quad (2.6)$$

Define $\rho^s(\mathbf{X}, t)$ to be the mass density of the solid skeleton in the reference configuration; $\rho^\beta(\mathbf{X}, t)$, $\beta = f, +, -$, stands for the partial mass density of the β -th constituent referring to the unit volume of the reference configuration of the skeleton; the quantity $\varphi^\alpha(\mathbf{X}, t)$ is the volume fraction of the α -th constituent. Physically φ^α represents the volume of the α -th constituent per unit volume of the mixture in the reference configuration.

The above equations are related to their Eulerian counterparts in the following way

$$\begin{aligned} \rho^{\alpha,t}(\mathbf{x}, t) &:= \rho^\alpha(\chi^{-1}(\mathbf{x}, t), t) J^{-1}(\chi^{-1}(\mathbf{x}, t), t), \\ \varphi^{\alpha,t}(\mathbf{x}, t) &:= \varphi^\alpha(\chi^{-1}(\mathbf{x}, t), t). \end{aligned} \quad (2.7)$$

Before stating the balance and constitutive equations, consider the following assumptions:

1. The mixture is incompressible. This means that all constituents are incompressible. In fact, incompressible mixtures have the property that the volume occupied by a given mass of component β in Ω_{t_0} equals the volume occupied by the same mass in Ω_t .
2. We assume that no chemical reactions exist between phases and no sources or sinks exit.
3. We neglect the inertia effects and body forces.
4. The materials are assumed to be isothermal.

5. Saturation assumption:

$$\varphi^s + \varphi^f = 1. \quad (2.8)$$

In fact, in the above relation, we use the fact that $\varphi^+ + \varphi^- \ll 1$.

6. It is assumed that the solid matrix is entirely elastic and initially isotropic. The solid deformation is assumed to be small enough so that the infinitesimal elasticity assumption is valid. The shear stress associated with mixture deformation is assumed to be negligible in the fluid phase. We also assume that the porous medium is initially homogenous and therefore φ^s is initially uniform. For our binary porous medium $\varphi^s = 1 - \varphi^f$.

Conservation equations for each constituent implies

$$\frac{\partial \Phi^\alpha}{\partial t} + \text{Div}(\Phi^\alpha \dot{\mathbf{x}}^{\alpha s}) = 0, \quad \alpha = s, f, +, -, \quad (2.9)$$

where 'Div' is the divergence operator in the reference configuration and $\Phi^\alpha := J\varphi^\alpha$. The mass flux is measured per unit of area of the reference configuration for the solid phase. Equation (2.9) for $\alpha = s$ gives

$$J\varphi^s = \varphi_0^s, \quad (2.10)$$

with φ_0^s is the initial volume fraction of solid phase. Equation (2.10) together with the saturation assumption (2.8) implies

$$\varphi^f = 1 - \varphi^s = 1 - \frac{1 - \varphi_0^f}{J}. \quad (2.11)$$

Since the solid phase is assumed to have infinitesimal deformation, the Taylor linearisation for J^{-1} at $\mathcal{F} = \mathbf{I}$ implies

$$J^{-1} \approx 1 - \left(\frac{1}{J^2} \frac{\partial J}{\partial \mathcal{F}} \right) \Big|_{\mathcal{F}=\mathbf{I}} : (\mathcal{F} - \mathbf{I}) = 1 - \text{Div} \mathbf{U},$$

where $\mathbf{U}(\mathbf{X}, t) := \chi(\mathbf{X}, t) - \mathbf{X}$ is the displacement vector of the solid phase. In the above relation, we use $\mathcal{F} = \mathbf{I} + \text{Grad} \mathbf{U}$ and

$$\frac{\partial J}{\partial \mathcal{F}} = J\mathcal{F}^{-T}. \quad (2.12)$$

After inserting the linearized form of J^{-1} into (2.11) we have

$$\varphi^f = 1 - (1 - \varphi_0^f)(1 - \text{Div} \mathbf{U}). \quad (2.13)$$

As a consequence of this formula, we have

$$\Phi^f = \varphi_0^f + \text{tr} \mathcal{E}(\mathbf{U}). \quad (2.14)$$

The momentum balance reads as:

$$\text{Div} \mathcal{P}(\mathbf{X}, t) = \mathbf{0}, \quad (2.15)$$

where \mathcal{P} is the first Piola-Kirchhoff stress tensor [7] and is given by the constitutive equation

$$\mathcal{P} = \mathcal{P}_0 + J(2\mu_s \mathcal{E}(\mathbf{U}) + (\lambda_s \text{tr} \mathcal{E}(\mathbf{U}) - p)\mathbf{I}) \mathcal{F}^{-T}. \quad (2.16)$$

In the above equation, $p(\mathbf{X}, t)$ is the fluid pressure and the strain tensor \mathcal{E} is defined by

$$\mathcal{E}(\mathbf{X}, t) = \frac{1}{2} (\text{Grad } \mathbf{U} + (\text{Grad } \mathbf{U})^T). \quad (2.17)$$

Electroneutrality requires

$$z^+ c^+ + z^- c^- + z^{fc} c^{fc} = 0, \quad (2.18)$$

where z^β , $\beta = +, -$, is the valence of the dissolved ion β . For a mono-valent salt, $z^+ = 1$ and $z^- = -1$. The superscript fc stands for fixed charge, i.e., the attached ionic group, thus c^{fc} denotes the molar concentration of the attached ions per unit fluid volume.

The conservation of fixed charge in the Lagrangian form reads

$$\varphi^f c^{fc} = \varphi_0^f c_0^{fc} J^{-1}, \quad (2.19)$$

where c_0^{fc} is the initial fixed charge concentration. Hence the electroneutrality condition in the initial state takes the following form

$$\frac{z^+ \Phi^+}{\bar{V}^+} + \frac{z^- \Phi^-}{\bar{V}^-} + z^{fc} \varphi_0^f c_0^{fc} = 0. \quad (2.20)$$

Note that

$$\bar{V}^\beta c^\beta = \frac{\varphi^\beta}{\varphi^f}, \quad (2.21)$$

therefore after differentiating in time the electroneutrality condition (2.20) can be written as:

$$\sum_{\beta=+,-} F \frac{z^\beta}{\bar{V}^\beta} \frac{\partial \Phi^\beta}{\partial t} = \epsilon \frac{\partial \xi}{\partial t}, \quad (2.22)$$

where $\xi(\mathbf{X}, t)$ is the voltage and $\epsilon > 0$ is a small departure from electroneutrality. In fact, this assumption is needed for a mathematical reason.

Based on [8], the constitutive equation to comply the second law of thermodynamics is given by

$$-\varphi^\beta \text{Grad } \mu^\beta = \sum_{\gamma=f,+, -} B^{\beta\gamma} \mathcal{F}^T \mathcal{F} \dot{\mathbf{x}}^{\gamma s}, \quad \beta = f, +, -, \quad (2.23)$$

where $\mathbf{B} = (B^{\beta\gamma})_{\beta,\gamma=f,+, -}$, is the friction matrix and $\mu^\beta(\mathbf{X}, t)$ is the electro-chemical potential of the constituent β , $\beta = f, +, -$. Based on [11], \mathbf{B} is defined as

$$\mathbf{B} = \begin{pmatrix} \frac{(\varphi^f)^2}{K} + (1-r)^2 B^{++} + (1-r)^2 B^{--} & -(1-r)B^{++} & -(1-r)B^{--} \\ -(1-r)B^{++} & B^{++} & 0 \\ -(1-r)B^{--} & 0 & B^{--} \end{pmatrix}, \quad (2.24)$$

and

$$\mu^f = p + \frac{\partial \mathcal{W}}{\partial \Phi^f}, \quad (2.25)$$

$$\mu^\beta = p + \frac{z^\beta F \xi}{V^\beta} + \frac{\partial \mathcal{W}}{\partial \Phi^\beta}, \quad \beta = +, -. \quad (2.26)$$

In the above relation, $B^{++}, B^{--} > 0$; $0 \leq r \leq 1$ is the hindrance factor and it is assumed to contain all physical phenomena reducing ionic diffusion rate and identical for cation and anion diffusion; W is the Helmholtz free energy of the porous medium. For such a mixture that consists of four components, the Helmholtz energy \mathcal{W} is expressed as a sum of elastic energy and a mixing energy for β -th constituent, $\beta = f, +, -$. Therefore

$$\begin{aligned} \mathcal{W}(\mathcal{F}^T \mathcal{F}, \Phi^f, \Phi^+, \Phi^-) &= \mathcal{W}_E(\mathcal{F}^T \mathcal{F}) + \mu_0^f \Phi^f + \mu_0^+ \Phi^+ + \mu_0^- \Phi^- \\ &+ RT(\Phi^f c - \frac{\Phi^+}{V^+} - \frac{\Phi^-}{V^-}) \left(\ln \frac{\Phi^f c - \frac{\Phi^+}{V^+} - \frac{\Phi^-}{V^-}}{\Phi^f c} - 1 \right) \\ &+ RT\Gamma \frac{\Phi^+}{V^+} \left(\ln \frac{\Phi^+}{\Phi^f c V^+} - 1 \right) \\ &+ RT\Gamma \frac{\Phi^-}{V^-} \left(\ln \frac{\Phi^-}{\Phi^f c V^-} - 1 \right). \end{aligned} \quad (2.27)$$

In this relation:

- μ_0^f is the initial electro-chemical potential of the fluid phase,
- μ_0^β is the initial electro-chemical potential of ion β ,
- $\Gamma \in (0, 1]$ is the osmotic coefficient of cation and anion, which is uniform and constant,
- c is the molar concentration of the fluid phase. Since ion concentrations are small, c is assumed to be uniform and constant,
- λ_s and μ_s are the Lamé stress constants,
- R is the universal gas constant,
- T is the absolute temperature, which is uniform and constant, since the state is assumed to be isothermal,
- \mathcal{W}_E is the elastic energy and is defined by

$$\mathcal{W}_E(\mathcal{F}^T \mathcal{F}) = \mathcal{W}_E(\mathcal{F}_0^T \mathcal{F}_0) + \frac{\lambda_s}{2} (\text{tr } \mathcal{E}(\mathbf{U}))^2 + \mu_s \mathcal{E}(\mathbf{U}) : \mathcal{E}(\mathbf{U}), \quad (2.28)$$

where \mathcal{F}_0 is the deformation of solid phase from stress-free configuration to initial configurations and is uniform in time.

With the prescribed energy \mathcal{W} , the relations (2.25) and (2.26) are postulated as

$$\mu^f = \mu_0^f + p - RT\Gamma(c^+ + c^-), \quad (2.29)$$

$$\mu^\beta = \mu_0^\beta + p + \frac{z^\beta F\xi}{V^\beta} + \frac{RT\Gamma}{V^\beta} \ln \frac{c^\beta}{c}, \quad \beta = +, -. \quad (2.30)$$

In the following lemma, we will show that the matrix \mathbf{B} is symmetric positive definite.

Lemma 2.1. \mathbf{B} is a symmetric positive definite matrix.

Proof. The symmetry property is trivial. Define diagonal matrix $\mathbf{D} = \text{diag}(1-r, 1, 1)$, then

$$\mathbf{D}^{-1}\mathbf{B}\mathbf{D}^{-1} = \begin{pmatrix} \frac{(\varphi^f)^2}{(1-r)^2 K} + B^{++} + B^{--} & -B^{++} & -B^{--} \\ -B^{++} & B^{++} & 0 \\ -B^{--} & 0 & B^{--} \end{pmatrix}. \quad (2.31)$$

The diagonal elements of $\mathbf{D}^{-1}\mathbf{B}\mathbf{D}^{-1}$ are all positive and the absolute value of each diagonal element is greater than the sum of absolute values of the non-diagonal elements in its row, therefore $\mathbf{D}^{-1}\mathbf{B}\mathbf{D}^{-1}$ is an irreducible diagonally dominant matrix, hence $\mathbf{D}^{-1}\mathbf{B}\mathbf{D}^{-1}$ is positive definite. This is enough to prove the positive definiteness of the matrix \mathbf{B} . \square

Note that from equation (2.23), we can obtain a relation for the fluxes $\Phi^\beta \dot{\mathbf{x}}^{\beta s}$ as:

$$\Phi^\beta \dot{\mathbf{x}}^{\beta s} = - \sum_{\gamma=f,+, -} \mathbf{P}^{\gamma s} \text{Grad } \mu^\gamma, \quad \beta = f, +, -, \quad (2.32)$$

where $\mathbf{P} = J\mathbf{N}(\mathcal{F}^T \mathbf{B} \mathcal{F})^{-1} \mathbf{N}$ and $\mathbf{N} = \text{diag}(\varphi^f, \varphi^+, \varphi^-)$.

Remark 2.2. Since the determinant of the deformation gradient \mathcal{F} is positive, based on lemma 2.1, \mathbf{B} is a symmetric positive definite matrix. Therefore \mathbf{P} is a symmetric positive definite matrix too.

Differentiating the equations (2.25) and (2.26) in time and using the fact that the energy function $\mathcal{W} = \mathcal{W}(\mathcal{E}, \Phi^\beta)$ gives:

$$\frac{\partial}{\partial t}(\mu^f - p) = \frac{\partial}{\partial \Phi^f} \left[\frac{\partial \mathcal{W}}{\partial \mathcal{E}} : \frac{\partial \mathcal{E}}{\partial t} + \sum_{\gamma=f,+, -} \frac{\partial \mathcal{W}}{\partial \Phi^\gamma} \frac{\partial \Phi^\gamma}{\partial t} \right], \quad (2.33)$$

$$\frac{\partial}{\partial t} \left(\mu^\beta - p - \frac{z^\beta F\xi}{V^\beta} \right) = \frac{\partial}{\partial \Phi^\beta} \left[\frac{\partial \mathcal{W}}{\partial \mathcal{E}} : \frac{\partial \mathcal{E}}{\partial t} + \sum_{\gamma=f,+, -} \frac{\partial \mathcal{W}}{\partial \Phi^\gamma} \frac{\partial \Phi^\gamma}{\partial t} \right]. \quad (2.34)$$

Observation of (2.27) reveals that the first term on the right hand side of the preceding two equations vanishes. This results into

$$\frac{\partial}{\partial t}(\mu^f - p) = \sum_{\gamma=f,+,-} W^{f\gamma} \frac{\partial \Phi^\gamma}{\partial t}, \quad (2.35)$$

$$\frac{\partial}{\partial t} \left(\mu^\beta - p - \frac{z^\beta F \xi}{V^\beta} \right) = \sum_{\gamma=f,+,-} W^{\beta\gamma} \frac{\partial \Phi^\gamma}{\partial t}, \quad \beta = +, -, \quad (2.36)$$

where $W^{\beta\gamma} = \frac{\partial^2 \mathcal{W}}{\partial \Phi^\beta \partial \Phi^\gamma}$ and $\mathbf{W} = (W^{\beta\gamma})_{\beta,\gamma=f,+,-}$.

Note that \mathbf{W} is a symmetric positive semi-definite matrix, indeed, from (2.29) and (2.30), the matrix \mathbf{W} is of the form

$$\mathbf{W} = RT\Gamma \begin{pmatrix} \frac{1}{(\Phi^f)^2} \left(\frac{\Phi^+}{V^+} + \frac{\Phi^-}{V^-} \right) & -\frac{1}{\Phi^f V^+} & -\frac{1}{\Phi^f V^-} \\ -\frac{1}{\Phi^f V^+} & \frac{1}{\Phi^+ V^+} & 0 \\ -\frac{1}{\Phi^f V^-} & 0 & \frac{1}{\Phi^- V^-} \end{pmatrix}. \quad (2.37)$$

Define diagonal matrix $\tilde{\mathbf{N}} = \text{diag}(\Phi^f, \Phi^+, \Phi^-)$, then

$$\tilde{\mathbf{N}}\mathbf{W}\tilde{\mathbf{N}} = RT\Gamma \begin{pmatrix} \left(\frac{\Phi^+}{V^+} + \frac{\Phi^-}{V^-} \right) & -\frac{\Phi^+}{V^+} & -\frac{\Phi^-}{V^-} \\ -\frac{\Phi^+}{V^+} & \frac{\Phi^+}{V^+} & 0 \\ -\frac{\Phi^-}{V^-} & 0 & \frac{\Phi^-}{V^-} \end{pmatrix}. \quad (2.38)$$

It is easy to see that $\tilde{\mathbf{N}}\mathbf{W}\tilde{\mathbf{N}}$ is symmetric positive semi-definite of rank two with zero eigenvectors $(1, 1, 1)^T$. Thus, \mathbf{W} is symmetric positive semi-definite of rank two.

The preceding relations can be written as:

$$\mathbf{W} \frac{\partial}{\partial t} \begin{pmatrix} \Phi^f \\ \Phi^+ \\ \Phi^- \end{pmatrix} = \frac{\partial}{\partial t} \begin{pmatrix} \mu^f \\ \mu^+ \\ \mu^- \end{pmatrix} - \mathbf{F} \frac{\partial}{\partial t} \begin{pmatrix} p \\ \xi \end{pmatrix}, \quad (2.39)$$

where

$$\mathbf{F} = \begin{pmatrix} 1 & 0 \\ 1 & \frac{Fz^+}{V^+} \\ 1 & \frac{Fz^-}{V^-} \end{pmatrix}. \quad (2.40)$$

In order to solve the above system of equations, we need to pose boundary conditions. This can be achieved by suitably combining the essential conditions for μ^f , μ^β and \mathbf{u} and the natural conditions for the normal components of \mathbf{q} , \mathbf{q}^β and $\boldsymbol{\sigma}$.

Consider the case that the porous medium is in contact with an electro-neutral bathing solution, given that the pressure p_{out} , the voltage ξ_{out} and the ion concentrations c_{out}

are known. The bathing solution contains no fixed charges, thus $c_{out}^+ = c_{out}^- = c_{out}$. Since the electro-chemical potentials are continuous at the boundary [8],

$$\mu_{in}^f = \mu_{out}^f, \quad (2.41)$$

$$\mu_{in}^+ = \mu_{out}^+, \quad (2.42)$$

$$\mu_{in}^- = \mu_{out}^-, \quad (2.43)$$

where μ_{out}^f and μ_{out}^β are the electro-chemical potentials in the outer solution. The combination of the above relations and the relations expressed in (2.25) and (2.26) provides

$$c_{in}^+ c_{in}^- = c_{out}^2, \quad (2.44)$$

$$\xi_{in} - \xi_{out} = \frac{RT}{F} \ln \frac{c_{out}^{\Gamma_{out}}}{(c_{in}^+)^{\Gamma}} c^{\Gamma - \Gamma_{out}}, \quad \beta = +, -. \quad (2.45)$$

In (2.45), $\xi_{in} - \xi_{out}$ describes the jump on the electrical potential, where Γ_{out} is the osmotic coefficient of the outer solution. It is called the Nernst potential, e.g. [5, 6]. By using the electroneutrality condition (2.18), we derive the Donnan equilibrium concentration of ions as

$$c_{in}^\beta = -\frac{1}{2z^\beta} z^f c^f c + \frac{1}{2} \sqrt{(z^f c^f c)^2 + 4c_{out}^2}, \quad \beta = +, -. \quad (2.46)$$

Now (2.25) yields

$$\pi := p_{in} - p_{out} = RT (\Gamma(c_{in}^+ + c_{in}^-) - 2c_{out}). \quad (2.47)$$

The variable π is the osmotic pressure [12]. We assume the osmotic coefficient of the external solution $\Gamma_{out} = 1$, therefore, using (2.29)-(2.30) we can derive the boundary values for the electro-chemical potentials μ_{in}^f and μ_{in}^β as

$$\mu_{in}^f = \mu_0^f + p_{out} - 2RT c_{out}, \quad (2.48)$$

$$\mu_{in}^\beta = \mu_0^\beta + p_{out} + \frac{Fz^\beta}{V^\beta} \xi_{out} + \frac{RT}{V^\beta} \ln \frac{c_{out}}{c}, \quad \beta = +, -. \quad (2.49)$$

3 One-Dimensional Configuration

In this section, we reduce the total set of equation to a one dimensional configuration. Equations (2.15) and (2.16) reduce to

$$(2\mu_s + \lambda_s) \frac{\partial^2 U}{\partial X^2} - \frac{\partial p}{\partial X} = 0. \quad (3.1)$$

Following [13], the momentum balance equation is integrated in the X -coordinate into

$$(2\mu_s + \lambda_s) \frac{\partial U}{\partial X} - p = f(t), \quad (3.2)$$

where $f(t)$ is the external load on the sample. In the experiment setup, 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 $\frac{\partial f(t)}{\partial t} = 0$. Hence, after differentiating (3.2) in t , we have

$$(2\mu_s + \lambda_s) \frac{\partial}{\partial t} \frac{\partial U}{\partial X} - \frac{\partial p}{\partial t} = 0. \quad (3.3)$$

The one-dimensional form of equation (2.14) gives $\Phi^f = \varphi_0^f + \frac{\partial U}{\partial X}$. Differentiating with respect to time gives

$$\frac{\partial \Phi^f}{\partial t} = \frac{\partial}{\partial t} \frac{\partial U}{\partial X}. \quad (3.4)$$

Then (3.3) converted to:

$$\frac{1}{2\mu_s + \lambda_s} \frac{\partial p}{\partial t} - \frac{\partial \Phi^f}{\partial t} = 0. \quad (3.5)$$

Combining this equation and the electroneutrality equation (2.22) results into:

$$\mathbf{H}_\epsilon \frac{\partial}{\partial t} \begin{pmatrix} p \\ \xi \end{pmatrix} = \mathbf{F}^T \frac{\partial}{\partial t} \begin{pmatrix} \Phi^f \\ \Phi^+ \\ \Phi^- \end{pmatrix}, \quad (3.6)$$

where

$$\mathbf{H}_\epsilon = \begin{pmatrix} 1/(2\mu_s + \lambda_s) & 0 \\ 0 & \epsilon \end{pmatrix}. \quad (3.7)$$

In this part, we assume that the matrix \mathbf{P} is constant. In fact, this assumption is made to linearize the problem. After substituting the constitutive equation (2.32) in the balance equation (2.9), we derive the following relation between Φ^β and μ^β

$$\frac{\partial}{\partial t} \begin{pmatrix} \Phi^f \\ \Phi^+ \\ \Phi^- \end{pmatrix} = \mathbf{P} \frac{\partial^2}{\partial X^2} \begin{pmatrix} \mu^f \\ \mu^+ \\ \mu^- \end{pmatrix}. \quad (3.8)$$

Now (2.39), (3.6) and (3.8) imply that

$$\frac{\partial}{\partial t} \begin{pmatrix} \mu^f \\ \mu^+ \\ \mu^- \end{pmatrix} = (\mathbf{W} + \mathbf{F}\mathbf{H}_\epsilon^{-1}\mathbf{F}^T) \mathbf{P} \frac{\partial^2}{\partial X^2} \begin{pmatrix} \mu^f \\ \mu^+ \\ \mu^- \end{pmatrix}. \quad (3.9)$$

If we define

$$\mathbf{E} = \mathbf{W} + \mathbf{F}\mathbf{H}_\epsilon^{-1}\mathbf{F}^T, \quad (3.10)$$

based on μ^β , the previous equation can be written as:

$$\frac{\partial}{\partial t} \begin{pmatrix} \mu^f \\ \mu^+ \\ \mu^- \end{pmatrix} = \mathbf{E}\mathbf{P} \frac{\partial^2}{\partial X^2} \begin{pmatrix} \mu^f \\ \mu^+ \\ \mu^- \end{pmatrix}. \quad (3.11)$$

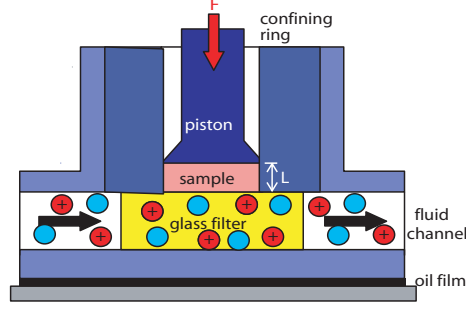


Figure 1: Schematic representation of the experimental set-up

Lemma 3.1. \mathbf{E} is a symmetric positive definite matrix.

Proof. It has been shown that \mathbf{W} is symmetric positive semi-definite of rank two with zero eigenvector $(\Phi^f, \Phi^+, \Phi^-)^T$. On the other hand, matrix $\mathbf{F}\mathbf{H}_c^{-1}\mathbf{F}^T$ with zero eigenvector $\left(\frac{Fz^+}{V^+} - \frac{Fz^-}{V^-}, \frac{Fz^-}{V^-}, -\frac{Fz^+}{V^+}\right)^T$ is symmetric positive semi-definite of rank two, therefore \mathbf{E} is symmetric positive definite. \square

In the next step, we modify the coupled system (3.11) by using the above lemma. Since \mathbf{E}^{-1} is a symmetric positive definite matrix, it can be decomposed into $\mathbf{E}^{-1} = \mathbf{G}^T\mathbf{G}$, where \mathbf{G} is a non-singular matrix. The matrix $\mathbf{A} = \mathbf{G}^{-T}\mathbf{P}\mathbf{G}^{-1}$ is symmetric positive definite, thus it decomposed as $\mathbf{A} = \mathbf{M}\mathbf{\Lambda}\mathbf{M}^{-1}$ where \mathbf{M} is a non-singular matrix corresponding to the eigenvectors of \mathbf{A} , and $\mathbf{\Lambda}$ a diagonal matrix corresponding to the eigenvalues of \mathbf{A} . Define $\mathbf{M}_1 = \mathbf{G}^{-1}\mathbf{M}$ and

$$\begin{pmatrix} \eta^f \\ \eta^+ \\ \eta^- \end{pmatrix} = \mathbf{M}_1^{-1} \begin{pmatrix} \mu^f \\ \mu^+ \\ \mu^- \end{pmatrix}, \quad (3.12)$$

then the coupled system (3.11) can be modified into:

$$\frac{\partial \eta^\beta}{\partial t} = \lambda^\beta \frac{\partial^2 \eta^\beta}{\partial X^2}, \quad \beta = f, +, -. \quad (3.13)$$

In the next section, separation of variables is used to obtain the analytical solutions of (3.13) for consolidation and free swelling.

4 Consolidation and free swelling experiments

In this section, the analytical solutions are derived for consolidation, free swelling and with respect to an initial steady reference state at $t = t_0$ assuming constant material parameters and small deformation. The homogeneous sample is placed frictionless in a holder. Figure 1 illustrates the experimental setup considered. 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 the top of the sample, $X = L$, where an external mechanical load is applied. The sample was made out of a hydrogel. A bathing solution flowed through a porous glass filter at the bottom of the sample.

4.1 Consolidation

In the consolidation experiment, we apply a load on the piston to be equal to $f(t) = -p_0\mathcal{H}(t - t_0)$, with $\mathcal{H}(t - t_0)$ the Heaviside function. We assume a sufficiently small value for p_0 to ensure that \mathbf{W} and \mathbf{P} are constant in time. The initial and boundary conditions for the displacement, fluid pressure, electrical potential and electro-chemical potentials with respect to the steady reference state $t = t_0$ are:

$$\begin{aligned} \mu^f(0, t) &= 0, & \mu^+(0, t) &= 0, & \mu^-(0, t) &= 0, \\ \frac{\partial \mu^f}{\partial X}(L, t) &= 0, & \frac{\partial \mu^+}{\partial X}(L, t) &= 0, & \frac{\partial \mu^-}{\partial X}(L, t) &= 0, \\ \mu^f(X, t_0) &= p_0, & \mu^+(X, t_0) &= 0, & \mu^-(X, t_0) &= 0, \\ p(0, t) &= 0, & p(X, t_0) &= p_0, & \xi(X, t_0) &= 0, \\ u(0, t) &= 0, & u(X, t_0) &= 0, & \xi(0, t) &= 0. \end{aligned} \quad (4.1)$$

The method of separation of variables is applied to solve (3.13) in corresponding with the boundary and initial conditions (4.1). The solutions are:

$$\begin{pmatrix} \mu^f(X, t) \\ \mu^+(X, t) \\ \mu^-(X, t) \end{pmatrix} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin\left(\frac{2n+1}{2} \frac{\pi}{L} X\right) \mathbf{M}_1 \mathbf{R}_n \mathbf{M}_1^{-1} \begin{pmatrix} p_0 \\ 0 \\ 0 \end{pmatrix}, \quad (4.2)$$

in which \mathbf{R}_n is a diagonal matrix with

$$\mathbf{R}_n^{ii} = \exp\left(-\left(\frac{2n+1}{2}\pi\right)^2 \frac{\lambda_i(t-t_0)}{L^2}\right), \quad i = f, +, -. \quad (4.3)$$

Using relation (3.6), (3.8) and (3.11) incorporates with the initial and boundary conditions on p and ξ gives:

$$\begin{pmatrix} p(X, t) \\ \xi(X, t) \end{pmatrix} = \mathbf{H}_\epsilon^{-1} \mathbf{F}^T \mathbf{E}^{-1} \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \times \sin\left(\frac{2n+1}{2} \frac{\pi}{L} \mathbf{X}\right) \mathbf{M}_1 (\mathbf{R}_n - \mathbf{I}) \mathbf{M}_1^{-1} \begin{pmatrix} p_0 \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} p_0 \\ 0 \end{pmatrix}, \quad (4.4)$$

where $\mathbf{\Lambda} = \text{diag}(\lambda^f, \lambda^+, \lambda^-)$.

The equations (3.2) and (4.4) in corporation of the boundary conditions gives:

$$\begin{aligned} U(X, t) &= \frac{1}{2\mu_s + \lambda_s} \begin{pmatrix} 1 & 0 \end{pmatrix} \mathbf{H}_\epsilon^{-1} \mathbf{F}^T \mathbf{E}^{-1} \frac{8L}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \\ &\quad \left(1 - \cos\left(\frac{2n+1}{2} \frac{\pi}{L} X\right)\right) \mathbf{M}_1 (\mathbf{R}_n - \mathbf{I}) \mathbf{M}_1^{-1} \begin{pmatrix} p_0 \\ 0 \\ 0 \end{pmatrix}. \end{aligned} \quad (4.5)$$

Given equations (2.32) and (4.2), the fluxes $\Phi^\beta \dot{x}^{\beta s}$, $\beta = f, +, -$ are equal to

$$\begin{pmatrix} \Phi^f \dot{x}^{fs}(X, t) \\ \Phi^+ \dot{x}^{+s}(X, t) \\ \Phi^- \dot{x}^{-s}(X, t) \end{pmatrix} = -\frac{2}{L} \sum_{n=0}^{\infty} \cos\left(\frac{2n+1}{2} \frac{\pi}{L} X\right) \mathbf{P} \mathbf{M}_1 \mathbf{R}_n \mathbf{M}_1^{-1} \begin{pmatrix} p_0 \\ 0 \\ 0 \end{pmatrix}. \quad (4.6)$$

4.2 Free Swelling

In the next experiment, we change the concentration of the external salt solution. According to (2.48), the following boundary and initial conditions for the free swelling experiment are considered

$$\begin{aligned} \mu^f(0, t) &= -2RT(\Delta c_{out}), & \frac{\partial \mu^f}{\partial X}(L, t) &= 0, & \mu^f(X, t_0) &= 0, \\ \mu^+(0, t) &= \frac{RT}{\bar{V}^+} \ln \frac{c_{out}(t_0^+)}{c_{out}(t_0^-)}, & \frac{\partial \mu^+}{\partial X}(L, t) &= 0, & \mu^+(X, t_0) &= 0, \\ \mu^-(0, t) &= \frac{RT}{\bar{V}^-} \ln \frac{c_{out}(t_0^+)}{c_{out}(t_0^-)}, & \frac{\partial \mu^-}{\partial X}(L, t) &= 0, & \mu^-(X, t_0) &= 0, \\ p(0, t) &= 0, & p(X, t_0) &= 0, & \xi(X, t_0) &= 0, \\ u(0, t) &= 0, & u(X, t_0) &= 0, & \xi(0, t) &= 0, \end{aligned} \quad (4.7)$$

in which Δc_{out} is the change in the external concentration and t_0^+ and t_0^- are the time just after and before 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 to be constant in time and secondly, the change of the electro-chemical potentials of the ions is approximately linear.

We follow the same outline as in the consolidation experiments to derive the solution of the equation (3.13) with the above initial and boundary conditions. This gives

$$\begin{pmatrix} \mu^f(X, t) \\ \mu^+(X, t) \\ \mu^-(X, t) \end{pmatrix} = \left[\mathbf{I} - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \times \sin\left(\frac{2n+1}{2} \frac{\pi}{L} X\right) \mathbf{M}_1 \mathbf{R}_n \mathbf{M}_1^{-1} \right] \begin{pmatrix} \mu^f(0, t) \\ \mu^+(0, t) \\ \mu^-(0, t) \end{pmatrix}, \quad (4.8)$$

$$\begin{pmatrix} p(X, t) \\ \xi(X, t) \end{pmatrix} = \mathbf{H}_\epsilon^{-1} \mathbf{F}^T \mathbf{E}^{-1} \quad (4.9)$$

$$\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin\left(\frac{2n+1}{2} \frac{\pi}{L} X\right) \mathbf{M}_1 (\mathbf{I} - \mathbf{R}_n) \mathbf{M}_1^{-1} \begin{pmatrix} \mu^f(0, t) \\ \mu^+(0, t) \\ \mu^-(0, t) \end{pmatrix},$$

$$U(X, t) = \frac{1}{2\mu_s + \lambda_s} \begin{pmatrix} 1 & 0 \end{pmatrix} \mathbf{H}_\epsilon^{-1} \mathbf{F}^T \mathbf{E}^{-1} \frac{8L}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \left(1 - \cos\left(\frac{2n+1}{2} \frac{\pi}{L} X\right) \right) \mathbf{M}_1 (\mathbf{I} - \mathbf{R}_n) \mathbf{M}_1^{-1} \begin{pmatrix} \mu^f(0, t) \\ \mu^+(0, t) \\ \mu^-(0, t) \end{pmatrix}. \quad (4.10)$$

Like the consolidation problem, the fluxes $\dot{x}^{\beta s}$ are derived and are equal to

$$\begin{pmatrix} \Phi^f \dot{x}^{fs}(X, t) \\ \Phi^+ \dot{x}^{+s}(X, t) \\ \Phi^- \dot{x}^{-s}(X, t) \end{pmatrix} = \frac{2}{L} \sum_{n=0}^{\infty} \cos\left(\frac{2n+1}{2} \frac{\pi}{L} X\right) \mathbf{P} \mathbf{M}_1 \mathbf{R}_n \mathbf{M}_1^{-1} \begin{pmatrix} \mu^f(0, t) \\ \mu^+(0, t) \\ \mu^-(0, t) \end{pmatrix}. \quad (4.11)$$

5 Results

In this section, the results for the consolidation and the free swelling are prescribed. As mentioned in the previous section, an uniaxial confined swelling and compression experiment performed on a cylindrical sample of cartilage substitute. This sample, with the diameter of 4 mm and the height of approximately 1 mm was put in an insulating confining ring. A piston on the top of the sample was loaded mechanically. A bathing solution flowed through a porous glass filter at the bottom of the sample. A change of the salt concentration of this solution generates a change in the boundary of ion concentrations and electro-chemical potentials as well as pressure and voltage.

During the experiment, the mechanical and chemical load were varied. Inspired by them, two numerical simulations are considered.

For both computations, the following parameters are considered:

$2\mu_s + \lambda_s = 4 * 10^3$ [MPa]	$c^{fc} = -0.2 * 10^{-4}$ [mol mm ⁻³]	$\varphi^f = 0.2$ [-]
$D^+ = 13.3 * 10^{-10}$ [m ² s ⁻¹]	$c_{out} = 1 * 10^{-4}$ [mol mm ⁻³]	$r = 0.4$ [-]
$D^- = 20.3 * 10^{-10}$ [m ² s ⁻¹]	$F = 96484.6$ [C mol ⁻¹]	$T = 293$ K
$K = 5.0 * 10^{-18}$ [m ⁴ N ⁻¹ s ⁻¹]	$\bar{V}^+ = 2.33 * 10^{-6}$ [m ³ mol ⁻¹]	$\Gamma = 0.9$ [-]
$R = 8.3145$ [J mol ⁻¹ K ⁻¹]	$\bar{V}^- = 15.17 * 10^{-6}$ [m ³ mol ⁻¹]	
$\epsilon = 10^{-12}$ [C ² N ⁻⁴ mm ⁴]		

Considering the above material parameters, the three eigenvalues in (3.13) are:

$$\begin{aligned} \lambda_1 &= 2.5279 \times 10^0 \text{ [m}^2 \text{ s}^{-1}\text{]}, \\ \lambda_2 &= 2.0510 \times 10^{-8} \text{ [m}^2 \text{ s}^{-1}\text{]}, \\ \lambda_3 &= 1.4906 \times 10^{-9} \text{ [m}^2 \text{ s}^{-1}\text{]}. \end{aligned}$$

For consolidation experiment, an inward force, $p_0 = 5$ MPa is applied to the left no-flow boundary, and at the right rigid boundary, the porous medium is in contact with an electro-neutral bathing solution. All boundary conditions are described in (4.1). Note that in this experiment, all the unknowns change immediately at $t = t_0$ s, thus another equilibrium will be establish in the end. At the final equilibrium, the electro-chemical potentials μ^β , $\beta = f, +, -$, have the same value as the value in the initial

state. However, the stress and fluid pressure have changed, since the porous medium is compressed. Figure 2 will display the solutions. As it can be seen the time for consolidation to occur is approximately $t - t_0 \approx 0.0417$ h.

For the free swelling experiment, the initial and boundary conditions are chosen from (4.7). In this experiment, we decrease the external salt concentration with a small amount from $c_{out} = 1 * 10^{-4}$ mol mm⁻³ to $c_{out} = 0.995 * 10^{-4}$ mol mm⁻³. Therefore, as on (2.49) μ^β changes accordingly. The displacement, pore pressure, electrical potential, electro-chemical potentials and ion concentrations are displayed in figure 3. The pore pressure increases from the initial value to the maximum value $p = 0.2922$ MPa at $t - t_0 \approx 0.0194$ h.

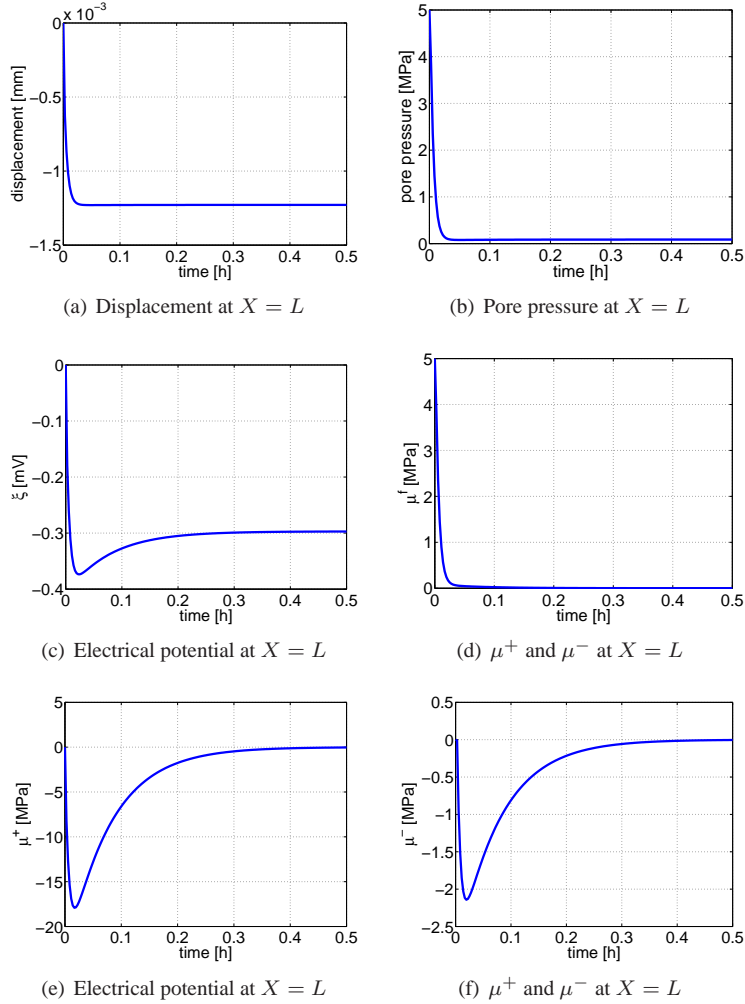


Figure 2: Results at $X = L$ for consolidation.

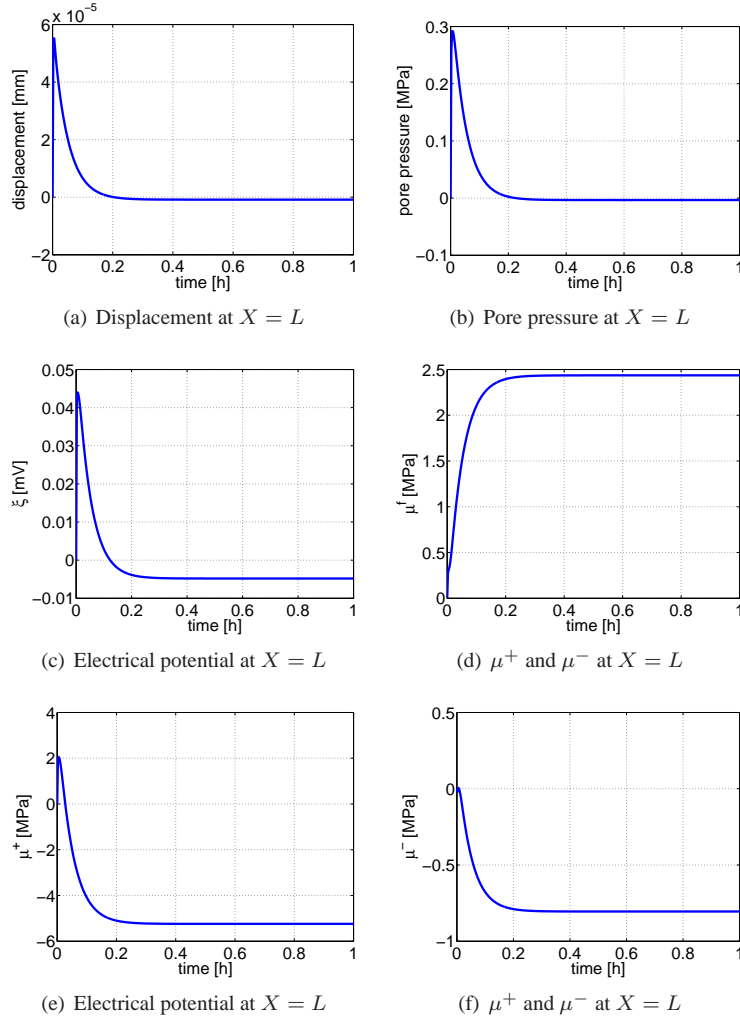


Figure 3: Results at $X = L$ for free swelling.

6 Conclusions

The analytical solutions are derived for consolidation and free swelling experiments to verify the numerical finite element solutions. The governing equations are defined in the Lagrangian coordinates. We assumed an infinitesimal deformation for the solid skeleton and a sufficiently small change in the external salt concentration. By choosing ϵ from interval $10^{-5} \leq \epsilon \leq 10^{-15}$ the results will remain same for both cases.

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