

MATHEMATICAL MODELLING AND NUMERICAL SOLUTION OF SWELLING OF CARTILAGINOUS TISSUES.

PART I: MODELLING OF INCOMPRESSIBLE CHARGED POROUS MEDIA *

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Abstract. The swelling and shrinkage of biological tissues are modelled by a four-component mixture theory in which a deformable and charged porous medium is saturated with a fluid with dissolved ions. Four components are defined: solid, liquid, cations and anions. The aim of this paper is the construction of the Lagrangian model of the four-component system. It is shown that, with the choice of Lagrangian description of the solid skeleton, the motion of the other components can be described in terms of Lagrangian initial system of the solid skeleton as well. Such an approach has a particularly important bearing on computer-aided calculations. Balance laws are derived for each component and for the whole mixture. In cooperation of the second law of thermodynamics, the constitutive equations are given. This theory results in a coupled system of nonlinear parabolic differential equations together with an algebraic constraint for electroneutrality. In this model, it is desirable to obtain an accurate approximation of the fluid flow and ions flow. Such an accurate approximation can be determined by the mixed finite element method. Part II is devoted to this task.

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Notation

a	scalar
\mathbf{a}, \mathbf{a}	vector
A	scalar
\mathbf{A}	matrix
\mathcal{A}	tensor
∇	gradient operator in current configuration
∇_0	gradient operator in initial configuration

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Nomenclature

\mathcal{C}	right Cauchy-Green strain tensor	[-]
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 charges attached to the solid skeleton per unit fluid volume	[mol·m ⁻³]
\mathcal{D}^β	diffusivity of ion β	[m ² ·s ⁻¹]
\mathcal{E}	Green strain tensor	[-]
f^β	activity coefficient of ion β	[-]
F	Faraday's constant	[C·mol ⁻¹]
\mathcal{K}	hydraulic permeability	[m ⁴ ·N ⁻¹ ·s ⁻¹]
p	pressure of the fluid phase	[N·m ⁻²]
\mathbf{q}^l	specific discharge relative to the solid	[m·s ⁻¹]
\mathbf{q}^β	flux of ion β relative to the fluid	[mol·m ⁻² ·s ⁻¹]
R	universal gas constant	[J·mol ⁻¹ ·K ⁻¹]
\mathcal{S}	second Piola-Kirchhoff stress	[N·m ⁻²]
t	time	[s]
T	absolute temperature	[K]
\mathbf{u}	displacement	[m]
\bar{V}^β	partial molar volume of ion β	[m ³ ·mol ⁻¹]
\mathbf{v}^α	velocity of the α -phase	[m·s ⁻¹]
\mathbf{v}^β	velocity of ion β	[m·s ⁻¹]
z^β	valance of ion β	[-]
z^{fc}	valance of fixed charge	[-]
$\boldsymbol{\sigma}$	Cauchy stress tensor	[N·m ⁻²]
λ_s	Lamé stress constant	[N·m ⁻²]
μ^l	electro-chemical potential of the fluid phase	[N·m ⁻²]
μ^β	electro-chemical potential of ion β	[J·mol ⁻¹]
μ_s	Lamé stress constant	[N·m ⁻²]
$\boldsymbol{\Pi}$	first Piola-Kirchhoff stress	[N·m ⁻²]
ξ	voltage	[V]
ρ^α	bulk density of the α -phase	[kg·m ⁻³]
ρ_T^α	true density of the α -phase	[kg·m ⁻³]
φ	volume fraction of the liquid phase	[-]
φ^α	volume fraction of the α -phase	[-]
φ^β	volume fraction of the component β	[-]
Γ^β	osmotic coefficient of ion β	[-]

1. INTRODUCTION

Many biological porous media exhibit swelling and shrinking behaviour when in contact with salt concentrations. This phenomenon, observed in cartilage and gels, is caused by electric charges fixed to the solid, counteracted by corresponding charges in fluid. These charges result in variety of features, including swelling, electro-osmosis, steaming potentials and streaming currents. We distinguish between the components and the phases in this way that the components are considered to be continua related to the same macroscopic volume measure for all components (in our case a solid, a liquid, anions, and cations) and phases are continua related to their own real volume measure (in our case solid and fluid). Mixture theory [2,3,6] is a framework, in which the model integrates mechanical deformations, loads, diffusion, convection and chemical reactions of different

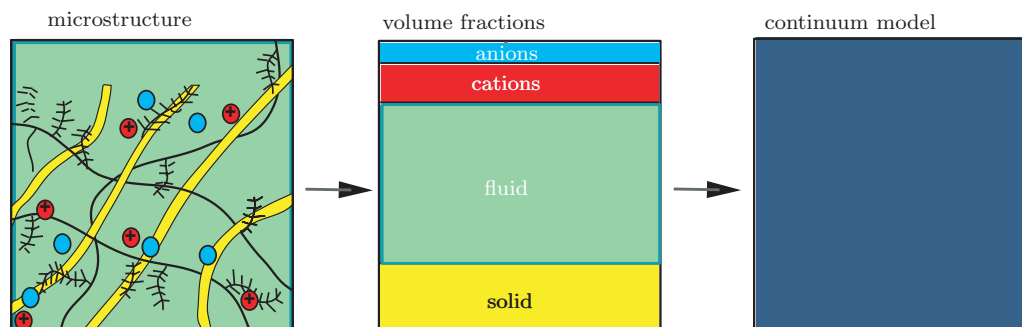


FIGURE 1. Micro-structure and macroscopic model.

solutes. An earlier study from geomechanics presents a biphasic models, which describes the solid-fluid interactions. These models can not describe osmotic effects, which have a major influence on the behaviour of tissues. Therefore to account for osmotic effects this is modelled by a triphasic model [8,14] and four-component mixture theory [4,7,12]. In the four-component mixture theory deformable and charged porous medium is saturated with a fluid with dissolved cations and anions. In this article we follow the outlines of the four-component model in more detail with an extension to Lagrangian formulation.

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 fluid pressure, ion concentrations or voltage results in flow of the fluid and ions [7].

In this paper, we construct the model of four-component porous material in Lagrangian coordinates of the skeleton. Such a description, particularly useful in computer-aided solutions, has not been used yet for multi-phase systems where the skeleton is usually described in Lagrangian coordinates and the other components in Eulerian coordinates.

This paper is outlined as follows: In the next section, we present the kinematic consideration and the balance laws. Section 3 is devoted to constitutive equations. In Section 4 we present the set of field equations for the Lagrangian description for the four-component system. In some detail, the transformation of the equations to the initial configuration of the skeleton is discussed. The fifth section is devoted to the Donnan equilibrium and boundary conditions.

2. BALANCE EQUATIONS

The swelling and shrinking behaviour of cartilaginous tissues (like intervertebral disc) can be modelled by a four-component mixture theory in which a deformable and charged porous medium is saturated with a fluid with dissolved ions. 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 components: liquid, cation and anion. We use the abbreviation s and f respectively for the solid phase and the fluid phase. The symbols l , $+$ and $-$ stand for liquid, cation and anion, respectively (*cf.* Fig. 1).

Definition 2.1. Consider a porous media with the components $\alpha = s, l, +$ and $-$. The kinematics in the mixture theory are based on two fundamental assumptions [2]:

- Each spatial point \mathbf{x} of the actual placement is simultaneously occupied by material points \mathbf{X}^α of all constituents $\alpha = s, f, +, -$ at the time t . The material points proceed from different initial positions \mathbf{X}^α at time $t = t_0$.

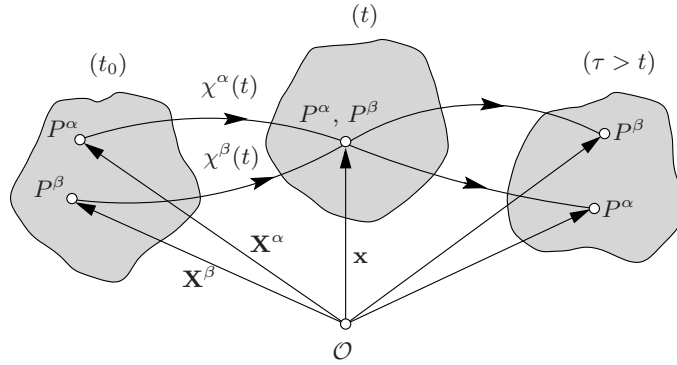


FIGURE 2. Motion of a multi-component mixture.

- Each constituent is assigned an independent state of motion.

Define the motion

$$\mathbf{x} = \chi^\alpha(\mathbf{X}^\alpha, t) : \Omega^\alpha \times [0, T] \rightarrow \Omega, \alpha = s, l, +, -, \tag{2.1}$$

where Ω is the domain occupied by the mixture and Ω^α represents the initial configuration of the α -component, \mathbf{X}^α is the position of the particle of the α -component in its initial configuration, t is the time and \mathbf{x} is the position occupied at time t by the particle labeled \mathbf{X}^α . At each time $t \in [0, T]$, the mappings are assumed to be one-to-one and sufficiently smooth to render the various mathematical operations meaningful. A geometrical interpretation of the motion function (2.1), concerning the motion of a solid and a fluid particle, is shown in Figure 2. Define the deformation gradient of the phase α by

$$\mathcal{F}^\alpha = \nabla_{\mathbf{X}^\alpha} \chi^\alpha = \frac{\partial \chi^\alpha}{\partial \mathbf{X}^\alpha}. \tag{2.2}$$

The determinant of the deformation gradient is defined as follow

$$J^\alpha = \det \mathcal{F}^\alpha. \tag{2.3}$$

Definition 2.2. The true density for the α -component is defined as the mass of the α -component per unit volume of the α -component and is denoted by ρ_T^α . The bulk density ρ^α to be the mass of the α -component per unit volume of the mixture. The quantity

$$\varphi^\alpha(\mathbf{x}, t) = \frac{\rho^\alpha(\mathbf{x}, t)}{\rho_T^\alpha(\mathbf{x}, t)} \tag{2.4}$$

is called the volume fraction of the α -component. Physically φ^α represents the volume of the α component per unit volume of the mixture.

The velocity of \mathbf{X}^α is defined by

$$\mathbf{v}^\alpha = \frac{\partial \chi^\alpha}{\partial t}(\mathbf{X}^\alpha, t). \tag{2.5}$$

The density of the mixture is defined by

$$\rho = \sum_{\alpha=s,l,+, -} \rho^\alpha. \tag{2.6}$$

The velocity of the mixture \mathbf{v} is defined by

$$\mathbf{v} = \frac{1}{\rho} \sum_{\alpha=s,l,+, -} \rho^\alpha \mathbf{v}^\alpha. \tag{2.7}$$

If Ψ is any function of \mathbf{x} and t , the derivatives of Ψ following the motion generated by \mathbf{v} and \mathbf{v}^α are, respectively

$$\frac{D\Psi}{Dt} = \frac{\partial\Psi}{\partial t} + \nabla\Psi \cdot \mathbf{v}, \tag{2.8}$$

$$\frac{D^\alpha\Psi}{Dt} = \frac{\partial\Psi}{\partial t} + \nabla\Psi \cdot \mathbf{v}^\alpha. \tag{2.9}$$

Definition 2.3. Define right Cauchy-Green strain tensor \mathbf{C} and Green strain tensor \mathbf{E} by

$$\mathbf{C} = (\mathcal{F}^s)^T \mathcal{F}^s, \tag{2.10}$$

$$\mathbf{E} = \frac{1}{2}(\mathbf{C} - \mathbf{I}). \tag{2.11}$$

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

- (1) The mixture is incompressible, which means that both fluid and solid are incompressible. Hence ρ_T^α is uniform in position and constant in time. In other words, volumetric changes of the porous medium are taken into account.
- (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) The mixture is assumed to be saturated, *i.e.*,

$$\varphi^s + \varphi^f = 1. \tag{2.12}$$

The volume fraction of the ions is neglected compared to those of the solid and the fluid (dilute solution),

$$\varphi^+ + \varphi^- \approx 0 \implies \varphi^f = \sum_{\beta=l,+,-} \varphi^\beta \approx \varphi^l. \tag{2.13}$$

- (6) It is assumed that the solid matrix is entirely elastic and initially isotropic. The shear stress associated with mixture deformation is assumed to be negligible in the fluid phase. We assume that the porous medium is initially homogenous and therefore φ^s is initially uniform. For our binary porous medium $\varphi = \varphi^f \approx \varphi^l$ indicates porosity and note that $\varphi^s = 1 - \varphi$.

Conservation of mass for the phases s and f imply

$$\frac{\partial\varphi^\alpha}{\partial t} + \nabla \cdot (\varphi^\alpha \mathbf{v}^\alpha) = 0, \quad \alpha = s, f. \tag{2.14}$$

Summing up these two equations for $\alpha = s, f$ and using the saturation assumption (2.12), the incompressible constraint condition reads

$$\nabla \cdot (\mathbf{q}^l + \mathbf{v}^s) = 0, \tag{2.15}$$

where the specific discharge relative to the solid phase is defined by

$$\mathbf{q}^l = \varphi(\mathbf{v}^f - \mathbf{v}^s). \tag{2.16}$$

The fluid velocity is a weighed average of the velocity of the liquid and the velocities of the ions. Since we are interested on the situation in which there are far more water molecules than ions, we approximate the velocity of the fluid by the velocity of the liquid, $\mathbf{v}^f \approx \mathbf{v}^l$.

The conservation of mass for the dissolved ions implies

$$\frac{\partial\varphi c^\beta}{\partial t} + \nabla \cdot (\varphi c^\beta \mathbf{v}^\beta) = 0, \quad \beta = +, -, \tag{2.17}$$

where c^β is the molar concentration of ion β per unit fluid volume and \mathbf{v}^β is the average velocity of ion β . Define the molar flux \mathbf{q}^β relative to the fluid as

$$\mathbf{q}^\beta = \varphi c^\beta (\mathbf{v}^\beta - \mathbf{v}^l). \quad (2.18)$$

After neglecting body forces and inertia effects, the momentum balance takes the form

$$\nabla \cdot \boldsymbol{\sigma}^\alpha + \boldsymbol{\pi}^\alpha = \mathbf{0}, \quad \alpha = s, l, +, -, \quad (2.19)$$

where $\boldsymbol{\sigma}^\alpha$ is the partial stress tensor of component α , $\boldsymbol{\pi}^\alpha$ is the momentum interaction with component other than α . The momentum balance for the mixture reads

$$\boldsymbol{\pi}^s + \boldsymbol{\pi}^l + \boldsymbol{\pi}^+ + \boldsymbol{\pi}^- = \mathbf{0}. \quad (2.20)$$

Hence

$$\nabla \cdot \boldsymbol{\sigma} = \nabla \cdot \boldsymbol{\sigma}^s + \nabla \cdot \boldsymbol{\sigma}^l + \nabla \cdot \boldsymbol{\sigma}^+ + \nabla \cdot \boldsymbol{\sigma}^- = \mathbf{0}, \quad (2.21)$$

where $\boldsymbol{\sigma}$ represents the Cauchy stress tensor of the mixture.

The balance of moment of momentum requires that the stress tensor $\boldsymbol{\sigma}$ be symmetric. The partial stresses $\boldsymbol{\sigma}^\alpha$ are symmetric if no moment of momentum interaction between components occurs (a proof can be found in [1]). In this work we shall assume all partial stresses to be symmetric.

Electroneutrality requires

$$z^+ c^+ + z^- c^- + z^{fc} c^{fc} = 0, \quad (2.22)$$

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 ions attached to the solid skeleton per unit fluid volume.

The conservation of fixed charge reads

$$\frac{\partial \varphi c^{fc}}{\partial t} + \nabla \cdot (\varphi c^{fc} \mathbf{v}^s) = 0. \quad (2.23)$$

Following the isothermal and incompressible conditions, the entropy inequality for a unit volume of mixture reads [1]:

$$\sum_{\alpha=s,l,+,-} \left(-\varphi^\alpha \frac{D^\alpha \Psi^\alpha}{Dt} + \boldsymbol{\sigma}^\alpha : \nabla \mathbf{v}^\alpha - \boldsymbol{\pi}^\alpha \cdot \mathbf{v}^\alpha \right) \geq 0, \quad (2.24)$$

where Ψ^α is the free energy density for the α -component per unit volume component and is defined by $\varphi^\alpha \Psi^\alpha = \psi^\alpha$ with ψ^α to be the Helmholtz free energy of component α per unit mixture volume, and \mathcal{D}^α is the symmetric part of the velocity gradient of the α -component.

Define W to be the Helmholtz free energy of the mixture by

$$W = J^s \sum_{\alpha=s,l,+,-} \varphi^\alpha \Psi^\alpha = J^s \sum_{\alpha=s,l,+,-} \psi^\alpha. \quad (2.25)$$

We try to rewrite the entropy inequality (2.24) per initial mixture volume. Note that

$$\frac{D^s J^s}{Dt} = J^s \nabla \cdot \mathbf{v}^s. \quad (2.26)$$

Material time differentiation of W with respect to the solid motion gives

$$\frac{D^s W}{Dt} = W \nabla \cdot \mathbf{v}^s + J^s \sum_{\alpha=s,l,+,-} \frac{D^s \varphi^\alpha}{Dt} \Psi^\alpha + J^s \sum_{\alpha=s,l,+,-} \varphi^\alpha \frac{D^s \Psi^\alpha}{Dt}. \quad (2.27)$$

Evidently,

$$\frac{D^s \Psi^\alpha}{Dt} = \frac{D^\alpha \Psi^\alpha}{Dt} + \nabla \Psi^\alpha \cdot (\mathbf{v}^s - \mathbf{v}^\alpha), \tag{2.28}$$

so,

$$\begin{aligned} -J^s \sum_{\alpha=s,l,+,-} \varphi^\alpha \frac{D^\alpha \Psi^\alpha}{Dt} &= -\frac{D^s W}{Dt} + W \nabla \cdot \mathbf{v}^s + J^s \sum_{\alpha=s,l,+,-} \frac{D^s \varphi^\alpha}{Dt} \Psi^\alpha \\ &\quad - J^s \sum_{\beta=l,+,-} \varphi^\beta \nabla \Psi^\beta \cdot (\mathbf{v}^\beta - \mathbf{v}^s). \end{aligned}$$

The definition of the material time derivative in (2.9) and the incompressibility assumption imply that

$$\begin{aligned} &+ J^s \sum_{\alpha=s,l,+,-} \frac{D^s \varphi^\alpha}{Dt} \Psi^\alpha \\ &= J^s \sum_{\alpha=s,f,+,-} \left(\Psi^\alpha \frac{\partial \varphi^\alpha}{\partial t} + \Psi^\alpha \nabla \varphi^\alpha \cdot \mathbf{v}^s \right) \\ &= J^s \sum_{\alpha=s,f,+,-} \left(\Psi^\alpha \frac{\partial \varphi^\alpha}{\partial t} + \Psi^\alpha (\nabla \cdot (\varphi^\alpha \mathbf{v}^s) - \varphi^\alpha \nabla \cdot \mathbf{v}^s) \right) \\ &= -J^s \nabla \cdot \mathbf{v}^s \sum_{\alpha=s,f,+,-} \Psi^\alpha \varphi^\alpha - J^s \sum_{\beta=l,+,-} \Psi^\beta \nabla \cdot (\varphi^\beta (\mathbf{v}^\beta - \mathbf{v}^s)) \\ &+ J^s \sum_{\alpha=s,l,+,-} \underbrace{\Psi^\alpha \left(\frac{\partial \varphi^\alpha}{\partial t} + \nabla \cdot (\varphi^\alpha \mathbf{v}^\alpha) \right)}_{=0} \\ &= -W \nabla \cdot \mathbf{v}^s - J^s \sum_{\beta=l,+,-} \Psi^\beta \nabla \cdot (\varphi^\beta (\mathbf{v}^\beta - \mathbf{v}^s)). \end{aligned}$$

Thus

$$-J^s \sum_{\alpha=s,l,+,-} \varphi^\alpha \frac{D^\alpha \Psi^\alpha}{Dt} = \frac{D^s W}{Dt} - J^s \sum_{\beta=s,l,+,-} \nabla \cdot (\Psi^\beta \varphi^\beta (\mathbf{v}^\beta - \mathbf{v}^s)). \tag{2.29}$$

By using equations (2.19) and (2.21) we have

$$\begin{aligned} \sum_{\alpha=s,l,+,-} \boldsymbol{\sigma}^\alpha : \nabla \mathbf{v}^\alpha &= \sum_{\alpha=s,l,+,-} \boldsymbol{\sigma}^\alpha \nabla \mathbf{v}^s + \sum_{\beta=l,+,-} \boldsymbol{\sigma}^\beta : \nabla (\mathbf{v}^\beta - \mathbf{v}^s) \\ &= \boldsymbol{\sigma} \nabla \mathbf{v}^s + \sum_{\beta=l,+,-} \nabla \cdot (\boldsymbol{\sigma}^\beta (\mathbf{v}^\beta - \mathbf{v}^s)) - \sum_{\alpha=s,l,+,-} \nabla \cdot \boldsymbol{\sigma}^\alpha \cdot \mathbf{v}^\alpha + \mathbf{v}^s \underbrace{\sum_{\alpha=s,l,+,-} \nabla \cdot \boldsymbol{\sigma}^\alpha}_0 \\ &= \boldsymbol{\sigma} \nabla \mathbf{v}^s + \sum_{\beta=l,+,-} \nabla \cdot (\boldsymbol{\sigma}^\beta (\mathbf{v}^\beta - \mathbf{v}^s)) + \sum_{\alpha=s,l,+,-} \boldsymbol{\pi}^\alpha \cdot \mathbf{v}^\alpha \end{aligned} \tag{2.30}$$

therefore by using the above results and equations (2.19) and (2.21) the entropy inequality (2.24) in the initial state of porous solid takes the following form

$$-\frac{D^s W}{Dt} + J^s \boldsymbol{\sigma} : \nabla \mathbf{v}^s - J^s \sum_{\beta=l,+,-} \nabla \cdot (\boldsymbol{\kappa}^\beta \cdot (\mathbf{v}^\beta - \mathbf{v}^s)) \geq 0, \tag{2.31}$$

where \mathcal{K}^β is the *chemical potential* tensor per unit mixture volume for the β -component and is defined by

$$\mathcal{K}^\beta = \psi^\beta \mathcal{I} - \boldsymbol{\sigma}^\beta, \quad \beta = l, +, -, \quad (2.32)$$

where \mathcal{I} is the second order unit tensor.

3. CONSTITUTIVE EQUATIONS

In order to complete the system of equations, it is necessary to provide constitutive equations for the specific discharge and the molar flux. Before we go through the details, we need to state some restrictions on the equations from the general continuum theory.

- Principle of material frame-indifference or objectivity, or in some literature known as principle of change of observer. This principle states that the response of any material must be independent of the observer.
- Principle of dissipation. This states that the constitutive relations must satisfy the reduced entropy inequality (2.31) for all values of their arguments [5].
- Principle of equipresence [16]. This states that if a variable is used in one constitutive relations of a problem, it should be used in all the constitutive relations for that problem (unless, its presence contradicts some other law or axiom).

Note that the entropy inequality should hold for all mixtures satisfying the balance laws, incompressibility and electroneutrality.

Due to the objectivity principle, we refer the current description of the mixture to the initial state of the porous solid. Define volume fractions

$$\Phi^\alpha = J^s \varphi^\alpha, \quad \alpha = s, l, +, -, \quad (3.1)$$

per unit initial volume, we can rewrite the balance equation (2.14) as follows:

$$\frac{D^s \Phi^\alpha}{Dt} + J^s \nabla \cdot (\varphi^\alpha (\mathbf{v}^\alpha - \mathbf{v}^s)) = 0, \quad \alpha = s, l, +, -. \quad (3.2)$$

We shall denote Φ^f by Φ . By introducing a Lagrange multiplier p for the incompressible constraint (2.15), the entropy inequality (2.31) takes the form

$$\begin{aligned} & - \frac{D^s W}{Dt} + J^s (\boldsymbol{\sigma} + p \mathcal{I}) : \nabla \mathbf{v}^s + J^s (-\mathcal{K}^l + p \varphi \mathcal{I}) : \nabla (\mathbf{v}^l - \mathbf{v}^s) \\ & + J^s \sum_{\beta=+,-} -\mathcal{K}^\beta : \nabla (\mathbf{v}^\beta - \mathbf{v}^s) + J^s (-\nabla \cdot \mathcal{K}^l + p \nabla \varphi) \cdot (\mathbf{v}^l - \mathbf{v}^s) \\ & + J^s \sum_{\beta=+,-} -\nabla \cdot \mathcal{K}^\beta \cdot (\mathbf{v}^\beta - \mathbf{v}^s) \geq 0. \end{aligned} \quad (3.3)$$

The electroneutrality condition (2.22) in the initial state takes the following form

$$\Phi z^+ c^+ + \Phi z^- c^- + z^{fc} \varphi_0 c_0^{fc} = 0, \quad (3.4)$$

where φ_0 and c_0^{fc} are initial porosity and initial fixed charge density, respectively. It is easy to check that

$$\frac{D^s \Phi c^\beta}{Dt} + J^s \nabla \cdot (\varphi c^\beta (\mathbf{v}^\beta - \mathbf{v}^s)) = 0, \quad \forall \beta = +, -. \quad (3.5)$$

After combining (3.4) and (3.5), we obtain another constraint for the entropy inequality as:

$$\sum_{\beta=+,-} \frac{1}{\bar{V}^\beta} \nabla \cdot (z^\beta \varphi^\beta (\mathbf{v}^\beta - \mathbf{v}^s)) = 0. \tag{3.6}$$

Here we use the fact that

$$\bar{V}^\beta c^\beta = \frac{\varphi^\beta}{\varphi}, \quad \beta = l, +, -, \tag{3.7}$$

where \bar{V}^β is the molar volume of the component β and is constant by incompressibility assumption, $\beta = l, +, -$ and $c^l = c - c^+ - c^-$. Here c is the molar concentration of the fluid phase, which is assumed to be uniform and constant.

The equation (3.6) can be written in another form as:

$$z^+ \nabla \cdot (\mathbf{q}^+ + c^+ \mathbf{q}^l) + z^- \nabla \cdot (\mathbf{q}^- + c^- \mathbf{q}^l) = 0. \tag{3.8}$$

In (3.5), the presence of molar volume \bar{V}^β shows a link between φ^β and φc^β . For the constitutive equations, our attempt is to introduce them not dependent on φ^β but on φc^β . As we will see later \bar{V}^β will help us to do it. Introducing the restriction equation (3.6) into inequality (3.3) by means of a Lagrange multiplier λ , yields:

$$\begin{aligned} & - \frac{D^s W}{Dt} + J^s (\boldsymbol{\sigma} + p \mathcal{I}) : \nabla \mathbf{v}^s + J^s (-\mathcal{K}^l + p \varphi \mathcal{I}) : \nabla (\mathbf{v}^l - \mathbf{v}^s) \\ & + J^s \sum_{\beta=+,-} \left(-\mathcal{K}^\beta + \frac{z^\beta \lambda}{\bar{V}^\beta} \varphi^\beta \mathcal{I} \right) : \nabla (\mathbf{v}^\beta - \mathbf{v}^s) \\ & + J^s (-\nabla \cdot \mathcal{K}^l + p \nabla \varphi) \cdot (\mathbf{v}^l - \mathbf{v}^s) \\ & + J^s \sum_{\beta=+,-} \left(-\nabla \cdot \mathcal{K}^\beta + \frac{z^\beta \lambda}{\bar{V}^\beta} \nabla \varphi^\beta \right) \cdot (\mathbf{v}^\beta - \mathbf{v}^s) \geq 0. \end{aligned} \tag{3.9}$$

To close the system, we choose W , $\boldsymbol{\sigma} + p \mathcal{I}$, $-\mathcal{K}^l + p \varphi \mathcal{I}$, $-\mathcal{K}^\beta + \varphi^\beta \lambda \frac{z^\beta}{\bar{V}^\beta} \mathcal{I}$ ($\beta = +, -$), $-\nabla \cdot \mathcal{K}^l + p \nabla \varphi$ and $-\nabla \cdot \mathcal{K}^\beta + \lambda \frac{z^\beta \varphi^\beta}{\bar{V}^\beta} \nabla \varphi^\beta$ ($\beta = +, -$) to be the constitutive variables, *i.e.*, they are functions of a set of independent variables (the constitutive variables are thus the dependent variables). We choose as independent variables the Green strain $\boldsymbol{\mathcal{E}}$ (*cf.* (2.11)), the Lagrangian form of the volume fractions of the liquid and the ions Φ^β , and of the relative velocities $\mathbf{v}^{\beta s} = (\mathcal{F}^s)^{-1}(\mathbf{v}^\beta - \mathbf{v}^s)$, $\beta = l, +, -$. Thus

$$W = W(\boldsymbol{\mathcal{E}}, \Phi^\beta, \mathbf{v}^{\beta s}), \tag{3.10}$$

$$\boldsymbol{\sigma} + p \mathcal{I} = \frac{1}{J^s} \mathcal{F}^s \tilde{\boldsymbol{\mathcal{S}}}(\boldsymbol{\mathcal{E}}, \Phi^\beta, \mathbf{v}^{\beta s}) (\mathcal{F}^s)^T, \tag{3.11}$$

$$-\mathcal{K}^l + p \varphi \mathcal{I} = \mathcal{F}^s \tilde{\mathcal{K}}^l(\boldsymbol{\mathcal{E}}, \Phi^\beta, \mathbf{v}^{\beta s}) (\mathcal{F}^s)^T, \tag{3.12}$$

$$-\mathcal{K}^\beta + \frac{z^\beta \lambda}{\bar{V}^\beta} \varphi^\beta \mathcal{I} = \mathcal{F}^s \tilde{\mathcal{K}}^\beta(\boldsymbol{\mathcal{E}}, \Phi^\beta, \mathbf{v}^{\beta s}) (\mathcal{F}^s)^T, \quad \beta = +, -, \tag{3.13}$$

$$-\nabla \cdot \mathcal{K}^l + p \nabla \varphi = \mathcal{F}^s \tilde{\mathcal{K}}^l(\boldsymbol{\mathcal{E}}, \Phi^\beta, \mathbf{v}^{\beta s}), \tag{3.14}$$

$$-\nabla \cdot \mathcal{K}^\beta + \frac{z^\beta \lambda}{\bar{V}^\beta} \nabla \varphi^\beta = \mathcal{F}^s \tilde{\mathcal{K}}^\beta(\boldsymbol{\mathcal{E}}, \Phi^\beta, \mathbf{v}^{\beta s}), \quad \beta = +, -. \tag{3.15}$$

We apply the chain rule for the time differentiation of W , hence we have

$$\begin{aligned} \frac{D^s W}{Dt} &= \frac{\partial W}{\partial \mathcal{E}} : \frac{D^s \mathcal{E}}{Dt} + \sum_{\beta=l,+,-} \frac{\partial W}{\partial \Phi^\beta} \frac{D^s \Phi^\beta}{Dt} + \sum_{\beta=l,+,-} \frac{\partial W}{\partial \mathbf{v}^{\beta s}} \cdot \frac{D^s \mathbf{v}^{\beta s}}{Dt} \\ &= \mathcal{F}^s \frac{\partial W}{\partial \mathcal{E}} (\mathcal{F}^s)^T : \mathcal{D}^s - J^s \sum_{\beta=l,+,-} \frac{\partial W}{\partial \Phi^\beta} \nabla \cdot (\varphi^\beta (\mathbf{v}^\beta - \mathbf{v}^s)) + \sum_{\beta=l,+,-} \frac{\partial W}{\partial \mathbf{v}^{\beta s}} \cdot \frac{D^s \mathbf{v}^{\beta s}}{Dt}. \end{aligned} \tag{3.16}$$

Here we use the fact that

$$\frac{D^s \mathcal{E}}{Dt} = (\mathcal{F}^s)^T \mathcal{D}^s \mathcal{F}^s.$$

We insert the equation (3.16) in (3.9). This results into

$$\begin{aligned} &\left(J^s (\boldsymbol{\sigma} + p \mathcal{I}) - \mathcal{F}^s \frac{\partial W}{\partial \mathcal{E}} (\mathcal{F}^s)^T \right) : \nabla \mathbf{v}^s - \sum_{\beta=l,+,-} \frac{\partial W}{\partial \mathbf{v}^{\beta s}} \cdot \frac{D^s \mathbf{v}^{\beta s}}{Dt} + J^s \left(-\boldsymbol{\kappa}^l + \left(p + \frac{\partial W}{\partial \Phi} \right) \varphi \mathcal{I} \right) : \nabla (\mathbf{v}^l - \mathbf{v}^s) \\ &+ J^s \sum_{\beta=+,-} \left(-\boldsymbol{\kappa}^\beta + \left(\frac{z^\beta \lambda}{\bar{V}^\beta} + \frac{\partial W}{\partial \Phi^\beta} \right) \varphi^\beta \mathcal{I} \right) : \nabla (\mathbf{v}^\beta - \mathbf{v}^s) + J^s \sum_{\beta=l,+,-} \mathbf{f}^\beta \cdot (\mathbf{v}^\beta - \mathbf{v}^s) \geq 0, \end{aligned} \tag{3.17}$$

where

$$\begin{aligned} \mathbf{f}^l &= -\nabla \cdot \boldsymbol{\kappa}^l + \left(p + \frac{\partial W}{\partial \Phi} \right) \nabla \varphi, \\ \mathbf{f}^\beta &= -\nabla \cdot \boldsymbol{\kappa}^\beta + \left(\frac{z^\beta \lambda}{\bar{V}^\beta} + \frac{\partial W}{\partial \Phi^\beta} \right) \nabla \varphi^\beta, \quad \beta = +, -. \end{aligned}$$

It follows from (3.10), (3.14) and (3.15) that

$$\mathbf{f}^\beta = \mathcal{F}^s \tilde{\mathbf{f}}^\beta (\mathcal{E}, \Phi^\beta, \mathbf{v}^{\beta s}), \quad \beta = l, +, -. \tag{3.18}$$

By a standard argument [5], (3.17) is satisfied if and only if

$$\boldsymbol{\sigma} + p \mathcal{I} = \frac{1}{J^s} \mathcal{F}^s \frac{\partial W}{\partial \mathcal{E}} (\mathcal{F}^s)^T, \tag{3.19}$$

$$\frac{\partial W}{\partial \mathbf{v}^{\beta s}} = 0, \quad \beta = l, +, -, \tag{3.20}$$

$$\boldsymbol{\kappa}^l = \left(p + \frac{\partial W}{\partial \Phi} \right) \varphi \mathcal{I}, \tag{3.21}$$

$$\boldsymbol{\kappa}^\beta = \left(\frac{z^\beta \lambda}{\bar{V}^\beta} + \frac{\partial W}{\partial \Phi^\beta} \right) \varphi^\beta \mathcal{I}, \quad \beta = +, -, \tag{3.22}$$

and

$$\sum_{\beta=l,+,-} \mathbf{f}^\beta \cdot (\mathbf{v}^\beta - \mathbf{v}^s) \geq 0. \tag{3.23}$$

Equation (3.19) shows that the stress of the mixture can be derived from the strain energy function W minus $p \mathcal{I}$. It can be seen that here p presents the hydrostatic pressure acting on the mixture [2]. Equation (3.20) shows

that the strain energy does not depend on the relative velocities. Define the chemical potential μ^l per unit fluid volume and the electro-chemical potential μ^β , $\beta = +, -$, per mol of ion β , such that

$$\mathcal{K}^l = \varphi \mu^l \mathcal{I}, \tag{3.24}$$

$$\mathcal{K}^\beta = \varphi c^\beta \mu^\beta \mathcal{I}, \quad \beta = +, -. \tag{3.25}$$

Therefore equation (3.21) and (3.22) imply that

$$\begin{aligned} \mu^l &= p + \frac{\partial W}{\partial \Phi^l}, \\ \mu^\beta &= \lambda z^\beta + \frac{\partial W}{\partial \Phi^\beta} \bar{V}^\beta, \quad \beta = +, -. \end{aligned} \tag{3.26}$$

It has been shown in [12] that the multiplier λ can be interpreted as the electrical potential of the medium multiplied by the constant of Faraday, *i.e.*, $\lambda = F\xi$.

We use of the residual inequality (3.23) to establish that

$$\tilde{\mathbf{f}}^\beta(\mathcal{E}, \Phi^\beta, \mathbf{0}) = \mathbf{0}, \quad \beta = l, +, -. \tag{3.27}$$

It is natural to refer to the state where $\mathbf{v}^{ls} = \mathbf{v}^{+s} = \mathbf{v}^{-s} = \mathbf{0}$ as the state of thermodynamic equilibrium. Equation (3.27) show that local interaction forces vanish in this state. In the approximation where the departures from the state GRAD $\Phi^\beta = \mathbf{0}$ and $\mathbf{v}^{\beta s} = \mathbf{0}$, for $\beta = l, +, -$, are assumed to be small, (3.18) can be approximated by

$$\mathbf{f}^\beta = \sum_{\gamma=l,+, -} B^{\beta\gamma}(\mathbf{v}^\gamma - \mathbf{v}^s), \quad \beta = l, +, -, \tag{3.28}$$

where

$$B^{\beta\gamma} = \mathcal{F}^s \frac{\partial \tilde{\mathbf{f}}^\beta}{\partial \mathbf{v}^{\gamma s}}(\mathcal{E}, \Phi^\gamma, \mathbf{0})(\mathcal{F}^s)^T, \quad \beta, \gamma = l, +, -. \tag{3.29}$$

Given (3.23) and (3.29), we can conclude that $B^{\beta\gamma}$ is a positive symmetric semi-definite matrix.

Substituting (3.26) into equation (3.28) yields the classical equations of irreversible thermodynamics:

$$\begin{cases} -\varphi^l \nabla \mu^l &= \sum_{\gamma=l,+, -} B^{l\gamma}(\mathbf{v}^\gamma - \mathbf{v}^s), \\ -\frac{\varphi^\beta}{\bar{V}^\beta} \nabla \mu^\beta &= \sum_{\gamma=l,+, -} B^{\beta\gamma}(\mathbf{v}^\gamma - \mathbf{v}^s), \quad \beta = +, -. \end{cases} \tag{3.30}$$

As it is assumed in the previous section, we restrict our considerations to isothermal, non-reacting mixtures where the solid phase is homogeneous. For such a mixture that consists of four components, the Helmholtz potential is expressed as a sum of an elastic energy $W(\mathcal{E})$ and a mixing energy $W(\Phi^\beta)$ for $\beta = l, +, -$. Also, we choose W to comply donnan equilibrium and van't Hoff equation. Therefore

$$\begin{aligned} W(\mathcal{E}, \Phi, \Phi^+, \Phi^-) &= (\mu_0^l + RTc)\Phi + \mu_0^+ \frac{\Phi^+}{\bar{V}^+} + \mu_0^- \frac{\Phi^-}{\bar{V}^-} \\ &+ RT\left(\Phi c - \frac{\Phi^+}{\bar{V}^+} - \frac{\Phi^-}{\bar{V}^-}\right) \left(\ln \frac{\Phi c - \frac{\Phi^+}{\bar{V}^+} - \frac{\Phi^-}{\bar{V}^-}}{\Phi c} - 1 \right) \\ &+ RT \Gamma^+ \frac{\Phi^+}{\bar{V}^+} \left(\ln \frac{\Phi^+}{\Phi c \bar{V}^+} - 1 \right) + RT \Gamma^- \frac{\Phi^-}{\bar{V}^-} \left(\ln \frac{\Phi^-}{\Phi c \bar{V}^-} - 1 \right) + W(\mathcal{E}). \end{aligned} \tag{3.31}$$

In this relation:

- μ_0^l is the initial electro-chemical potential of the fluid phase;
- μ_0^β is the initial electro-chemical potential of ion β ;
- $\Gamma^\beta \in (0, 1]$ is the osmotic coefficient of ion β , which is uniform and constant;
- c is the molar concentration of the fluid phase, which is assumed to be uniform and constant;
- R is the universal gas constant;
- T is the absolute temperature, which is uniform and constant since the materials are assumed to be isothermal.

The constitutive equations (3.19) and (3.30) that fulfill the second law of thermodynamics are

$$\boldsymbol{\sigma} + p\boldsymbol{\mathcal{I}} = \frac{1}{J_s} \mathcal{F}^s \frac{\partial W}{\partial \boldsymbol{\mathcal{E}}} (\mathcal{F}^s)^T, \quad (3.32)$$

$$-\varphi^\beta \nabla \tilde{\mu}^\beta = \sum_{\gamma=l,+,-} B^{\beta\gamma} (\mathbf{v}^\gamma - \mathbf{v}^s), \quad \beta = l, +, -, \quad (3.33)$$

with $\tilde{\mu}^l = \mu^l$, $\tilde{\mu}^\beta = \mu^\beta / \bar{V}^\beta$, ($\beta = +, -$).

By using equations (3.26) and (3.31) we simplify the equations for the electro-chemical potentials as

$$\begin{aligned} \mu^l = p + \frac{\partial W}{\partial \Phi} &= p + \mu_0^l + RTc \ln \left(\frac{\Phi c - \frac{\Phi^+}{\bar{V}^+} - \frac{\Phi^-}{\bar{V}^-}}{\Phi c} \right) + \frac{RT}{\Phi} \left(\frac{\Phi^+}{\bar{V}^+} + \frac{\Phi^-}{\bar{V}^-} \right) \\ &- \frac{RT \Gamma^+ \Phi^+}{\bar{V}^+ \Phi} - \frac{RT \Gamma^- \Phi^-}{\bar{V}^- \Phi}, \end{aligned} \quad (3.34)$$

and

$$\mu^\beta = z^\beta F\xi + \frac{\partial W}{\partial \Phi^\beta} \bar{V}^\beta = z^\beta F\xi + \mu_0^\beta - RT \ln \left(\frac{\Phi c - \frac{\Phi^+}{\bar{V}^+} - \frac{\Phi^-}{\bar{V}^-}}{\Phi c} \right) + RT \Gamma^\beta \ln \left(\frac{\Phi^\beta}{\Phi c \bar{V}^\beta} \right), \quad \beta = +, -. \quad (3.35)$$

After linearizing the logarithm terms and using (3.7) we have

$$\begin{aligned} \mu^l &\approx p + \mu_0^l - RT (\Gamma^+ c^+ + \Gamma^- c^-) \\ \mu^\beta &\approx \mu_0^\beta + z^\beta F\xi + RT \Gamma^\beta \ln \frac{c^\beta}{c}, \quad \beta = +, -. \end{aligned} \quad (3.36)$$

In [13], the components of the friction matrix are related to diffusion coefficients of fluid and ions and it can be shown as the followings:

$$B^{ll} := \varphi^2 K^{-1} - (B^{l+} + B^{l-}), \quad (3.37)$$

$$B^{ii} := -B^{il}, \quad i = +, -, \quad (3.38)$$

$$B^{il} := -\varphi^i RT (\bar{V}^i D^i)^{-1}, \quad i = +, -, \quad (3.39)$$

$$B^{+-} := \mathbf{0}, \quad (3.40)$$

where \mathcal{K} is the permeability and D^i is the ion diffusion tensor in free water. Manipulation of the second equation in (3.33) yields

$$\varphi^\beta (\mathbf{v}^\beta - \mathbf{v}^s) = - \sum_{\gamma=l,+,-} P^{\beta\gamma} \nabla \tilde{\mu}^\gamma, \quad \beta = l, +, -, \quad (3.41)$$

with

$$P^{\beta\gamma} = \varphi^\beta \varphi^\gamma (B^{-1})^{\beta\gamma}, \quad \beta, \gamma = l, +, -.$$

$\mathbf{P} = (P^{\beta\gamma})_{\beta, \gamma=l, +, -}$ can be derived as:

$$\mathbf{P} = \begin{pmatrix} K & K \frac{\varphi^+}{\varphi} & K \frac{\varphi^-}{\varphi} \\ K \frac{\varphi^+}{\varphi} & \frac{\bar{V}^+ D^+ \varphi^+}{RT} + K \left(\frac{\varphi^+}{\varphi}\right)^2 & K \frac{\varphi^+ \varphi^-}{\varphi^2} \\ K \frac{\varphi^-}{\varphi} & K \frac{\varphi^+ \varphi^-}{\varphi^2} & \frac{\bar{V}^- D^- \varphi^-}{RT} + K \left(\frac{\varphi^-}{\varphi}\right)^2 \end{pmatrix}. \tag{3.42}$$

Now by using (3.41) we can derive the specific discharge \mathbf{q}^l and the ion fluxes \mathbf{q}^i in terms of the electro-chemical potential μ^β

$$\begin{aligned} \mathbf{q}^l = \varphi(\mathbf{v}^l - \mathbf{v}^s) &= - \sum_{\gamma=l, +, -} P^{l\gamma} \nabla \tilde{\mu}^\gamma = - \frac{K}{\varphi} (\nabla \tilde{\mu}^l + \varphi^+ \nabla \tilde{\mu}^+ + \varphi^- \nabla \tilde{\mu}^-) \\ &= - K (\nabla \mu^l + c^+ \nabla \mu^+ + c^- \nabla \mu^-), \end{aligned} \tag{3.43}$$

and

$$\begin{aligned} \mathbf{q}^\beta &= \frac{\varphi^\beta}{\bar{V}^\beta} (\mathbf{v}^\beta - \mathbf{v}^l) = \frac{\varphi^\beta}{\bar{V}^\beta} (\mathbf{v}^\beta - \mathbf{v}^s) - \frac{\varphi^\beta}{\bar{V}^\beta} (\mathbf{v}^l - \mathbf{v}^s) = - \frac{1}{\bar{V}^\beta} \sum_{\gamma=l, +, -} P^{\beta\gamma} \nabla \tilde{\mu}^\gamma - c^\beta \mathbf{q}^l \\ &= - \frac{D^\beta c^\beta \varphi}{RT} \nabla \mu^\beta, \quad \beta = +, -. \end{aligned} \tag{3.44}$$

The above relations are called the extended Darcy’s law and Fick’s law.

Assuming the electroneutrality (2.22), if we put (3.36) into (3.43) and (3.44), then the extended Darcy’s law and the Fick’s law can be stated in terms of the variables p , c^β and ξ as follow:

$$\begin{aligned} \mathbf{q}^l &= - K (\nabla p - z^{fc} c^{fc} F \nabla \xi), \\ \mathbf{q}^\beta &= - D^\beta \varphi \left(\frac{F}{RT} z^\beta c^\beta \nabla \xi + \Gamma^\beta \nabla c^\beta \right), \quad \beta = +, -. \end{aligned} \tag{3.45}$$

From physical considerations [12], μ^l and μ^β are continuous even if c^{fc} is not. Therefore we choose the electro-chemical potentials to be the primal variables.

Remark 3.1. Define the activity f^β by

$$f^\beta = \left(\frac{c^\beta}{c} \right)^{\Gamma^{\beta-1}}, \quad \beta = +, -. \tag{3.46}$$

Then based on the definition of the electro-chemical potentials and on the electroneutrality assumption, the secondary variables c^β , p and ξ are expressed as

$$c^\beta = - \frac{1}{2z^\beta} z^{fc} c^{fc} + \frac{1}{2} \sqrt{(z^{fc} c^{fc})^2 + \frac{4c^2}{f^+ f^-} \exp \frac{\mu^+ - \mu_0^+ + \mu^- - \mu_0^-}{RT}}, \tag{3.47}$$

$$p = \mu^l - \mu_0^l + RT (\Gamma^+ c^+ + \Gamma^- c^-), \tag{3.48}$$

$$\xi = \frac{1}{z^\beta F} \left(\mu^\beta - \mu_0^\beta - RT \ln \frac{f^\beta c^\beta}{c} \right), \quad \beta = +, -. \tag{3.49}$$

The ion concentrations c^β are clearly positive. For numerical stability, it is preferable to use the expression for voltage with $\beta = -$ if z^{fc} is positive and *vice versa*.

4. REFORMULATION IN LAGRANGIAN COORDINATE

From now, we omit the superscript s from \mathcal{F}^s and J^s and $\frac{D^s}{Dt}$. Recall the Nanson’s formula [11], page 75, then obviously the following relations hold for the gradient and the divergence operators in the initial and the current configurations:

For a scalar a , a vector \mathbf{a} and a tensor \mathcal{T} :

$$\begin{aligned} \nabla_0 a &= \mathcal{F}^T \nabla a, \\ \frac{1}{J} \nabla_0 \cdot (J \mathcal{F}^{-1} \mathbf{a}) &= \nabla \cdot \mathbf{a}, \\ \frac{1}{J} \nabla_0 \cdot (J \mathcal{F}^{-1} \mathcal{T}) &= \nabla \cdot \mathcal{T}. \end{aligned}$$

Define φ_0 and $\varphi_0^s = 1 - \varphi_0$ as the initial porosity and the initial volume fraction of the solid phase, respectively. Recall the Lagrangian form of the balance equation (2.14) as it stated in (3.2)

$$\frac{DJ\varphi^\alpha}{Dt} + J\nabla \cdot (\varphi^\alpha(\mathbf{v}^\alpha - \mathbf{v}^s)) = 0, \quad \alpha = s, l, +, -.$$

Easily it can be seen that the above equation is equivalent to

$$\frac{DJ\varphi^\alpha}{Dt} + \nabla_0 \cdot (J\mathcal{F}^{-1}\varphi^\alpha(\mathbf{v}^\alpha - \mathbf{v}^s)) = 0, \quad \alpha = s, l, +, -.$$

For $\alpha = s$ we have

$$\frac{DJ\varphi^s}{Dt} = 0, \quad \text{or} \quad \varphi^s J = \varphi_0^s,$$

where φ_0^s is the solid volume fraction in the initial configuration. This gives

$$\varphi = 1 - \varphi^s = 1 - \frac{1 - \varphi_0}{J}. \tag{4.1}$$

For $\alpha = l$ we have

$$\frac{DJ\varphi}{Dt} + \nabla_0 \cdot \mathfrak{Q}^l = 0, \tag{4.2}$$

where

$$\mathfrak{Q}^l = J\mathcal{F}^{-1}\mathbf{q}^l. \tag{4.3}$$

By using definitions (2.16), (2.18) and equation (3.2), we have

$$\frac{DJ\varphi c^\beta}{Dt} + J\nabla \cdot (\mathbf{q}^\beta + c^\beta \mathbf{q}^l) = 0, \quad \beta = +, -.$$

Finally the ions balance in Lagrangian form takes the following form

$$\frac{DJ\varphi c^\beta}{Dt} + \nabla_0 \cdot (\mathfrak{Q}^\beta + c^\beta \mathfrak{Q}^l) = 0, \quad \beta = +, -, \tag{4.4}$$

where

$$\mathfrak{Q}^\beta = J\mathcal{F}^{-1}\mathbf{q}^\beta, \quad \beta = +, -. \tag{4.5}$$

In the Lagrangian form, (2.23) is expressed as

$$\frac{DJ\varphi c^{fc}}{Dt} = 0, \quad \text{or} \quad \varphi c^{fc} = \varphi_0 c_0^{fc} J^{-1}, \tag{4.6}$$

where c_0^{fc} is the fixed charge concentration in the initial configuration. From (4.1)

$$(\varphi J)^{-1} = (J - \varphi_0^s)^{-1}$$

and therefore

$$c^{fc} = c_0^{fc} \varphi_0 (J - \varphi_0^s)^{-1}. \tag{4.7}$$

Equation (2.21) in Lagrangian form takes the following form

$$\nabla_0 \cdot \mathbf{\Pi} = \mathbf{0} \quad \text{or} \quad \nabla_0 \cdot (\mathbf{S}\mathcal{F}^T) = \mathbf{0}, \tag{4.8}$$

where $\mathbf{\Pi}$ and \mathbf{S} are the first and second Piola-Kirchhoff stress tensors. The constitutive relation (3.32) is

$$\boldsymbol{\sigma} + p\mathbf{I} = \frac{1}{J}\mathcal{F}\frac{\partial W}{\partial \boldsymbol{\mathcal{E}}}\mathcal{F}^T.$$

Considering this relation, the second Piola-Kirchhoff stress is expressed by

$$\mathbf{S} = \mathbf{\Pi}\mathcal{F}^{-T} = \frac{\partial W}{\partial \boldsymbol{\mathcal{E}}} - pJ\mathbf{C}^{-1}, \tag{4.9}$$

where the right Cauchy-Green tensor \mathbf{C} is defined in (2.10).

It is easy to check that the Lagrangian forms of equations (3.43) and (3.44) are

$$\begin{aligned} \boldsymbol{\Phi}^l &= -\tilde{\mathcal{K}}(\nabla_0 \mu^l + c^+ \nabla_0 \mu^+ + c^- \nabla_0 \mu^-), \\ \boldsymbol{\Phi}^\beta &= -\frac{\tilde{\mathcal{D}}^\beta c^\beta \varphi}{RT} \nabla_0 \mu^\beta, \quad \beta = +, -, \end{aligned} \tag{4.10}$$

where

$$\tilde{\mathcal{K}} = J\mathcal{F}^{-1}\mathcal{K}\mathcal{F}^{-T}, \tag{4.11}$$

$$\tilde{\mathcal{D}}^\beta = J\mathcal{F}^{-1}\mathcal{D}^\beta\mathcal{F}^{-T}, \quad \beta = +, -. \tag{4.12}$$

5. TOTAL SET OF EQUATIONS

The combination of the deformation of the porous media and the flow of the fluid and ions in the Lagrangian description result into the following set of equations:

Balance equations	
$\nabla_0 \cdot (\mathcal{S}\mathcal{F}^T) = \mathbf{0},$	(5.1)
$\frac{DJ\varphi}{Dt} + \nabla_0 \cdot \mathfrak{Q}^l = 0,$	
$\frac{DJ\varphi c^\beta}{Dt} + \nabla_0 \cdot (\mathfrak{Q}^\beta + c^\beta \mathfrak{Q}^l) = 0, \quad \beta = +, -.$	
Constitutive equations	
$\frac{\partial W}{\partial \mathcal{E}} - pJ\mathcal{C}^{-1} = \mathcal{S},$	
$-\tilde{\mathcal{K}}(\nabla_0 \mu^l + c^+ \nabla_0 \mu^+ + c^- \nabla_0 \mu^-) = \mathfrak{Q}^l,$	
$-\frac{\tilde{\mathcal{D}}^\beta c^\beta \varphi}{RT} \nabla_0 \mu^\beta = \mathfrak{Q}^\beta, \quad \beta = +, -.$	

6. DONNAN EQUILIBRIUM AND BOUNDARY CONDITIONS

In order to solve the above system of equations, we need to pose the boundary conditions. This can be achieved by suitably combining the essential conditions for μ^l , μ^β and \mathbf{u} and the natural conditions for the normal components of \mathfrak{Q}^β , $\beta = l, +, -$ and \mathcal{S} .

Consider the case that the porous medium is in contact with an electroneutral 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,

$$\mu_{in}^l = \mu_{out}^l, \quad (6.1)$$

$$\mu_{in}^+ = \mu_{out}^+, \quad (6.2)$$

$$\mu_{in}^- = \mu_{out}^-, \quad (6.3)$$

where μ_{out}^l and μ_{out}^β are the electro-chemical potentials in the outer solution. Assume $\Gamma_{in}^+ = \Gamma_{in}^- = \Gamma$ and $\Gamma_{out}^+ = \Gamma_{out}^- = 1$, then the combination of the above relations and the relations expressed in (3.36) provides

$$\mu_{in}^l = \mu_0^l + p_{out} - 2RTc_{out}, \quad (6.4)$$

$$\mu_{in}^\beta = \mu_0^\beta + Fz^\beta \xi_{out} + RT\Gamma \ln \frac{c_{out}}{c}, \quad \beta = +, -, \quad (6.5)$$

where c_{out} , p_{out} and ξ_{out} are the ions concentration, fluid pressure and the electrical potential of the outer solution, respectively. Equation (6.5) for $\beta = +, -$ in combination with (6.2) and (6.3) imply

$$\mu_0^+ + \mu_0^- + RT \ln \frac{c_{out}^2}{c^2} = \mu_{out}^+ + \mu_{out}^- = \mu_{in}^+ + \mu_{in}^- = \mu_0^+ + \mu_0^- + RT \Gamma \ln \frac{c_{in}^+ c_{in}^-}{c^2}.$$

Therefore, we have

$$\frac{c_{out}^2}{c^2} = \left(\frac{c_{in}^+ c_{in}^-}{c^2} \right)^\Gamma. \quad (6.6)$$

Easily we can see that

$$\pi = p_{in} - p_{out} = RT (\Gamma(c_{in}^+ + c_{in}^-) - 2c_{out}), \tag{6.7}$$

$$\xi_{in} - \xi_{out} = \frac{RT}{Fz^\beta} \ln \frac{c_{out}c^{\Gamma-1}}{(c_{in}^\beta)^\Gamma}, \beta = +, -. \tag{6.8}$$

In (6.7), π is the osmotic pressure [15] and $\xi_{in} - \xi_{out}$ is the Donnan voltage between the inner and outer solution. It is called Nernst potential [9, 10].

Let Ω be an open domain in \mathbb{R}^n , $n = 1, 2, 3$, then define $\Omega_T = \Omega \times (0, T]$ for $T > 0$ and consider the sets $\Gamma_{\mathbf{u}}^D$ and $\Gamma_{\mathbf{u}}^N$ (and similarly Γ_p^D and Γ_p^N) to be two disjoint open subsets of the total boundary $\Gamma = \partial\Omega$, such that $\Gamma_\alpha^D \cap \Gamma_\alpha^N = \emptyset$ and $\bar{\Gamma}_\alpha^D \cup \bar{\Gamma}_\alpha^N = \Gamma$ for $\alpha = \mathbf{u}$ and p . We assume

$$\text{meas } \Gamma_\alpha^D > 0 \quad \text{for } \alpha = \mathbf{u}, p. \tag{6.9}$$

From the above statements we can get the following boundary conditions:

Boundary conditions		
\mathbf{u}	$= \mathbf{0}$	on $\Gamma_{\mathbf{u}}^D \times (0, T]$,
μ^l	$= \mu_{in}^l$	on $\Gamma_p^D \times (0, T]$,
μ^+	$= \mu_{in}^+$	on $\Gamma_p^D \times (0, T]$,
μ^-	$= \mu_{in}^-$	on $\Gamma_p^D \times (0, T]$,
$\mathbf{n} \cdot (\mathcal{S}\mathcal{F}^T)$	$= \mathbf{g}_{\mathbf{u}}^N$	on $\Gamma_{\mathbf{u}}^N \times (0, T]$,
$\mathbf{n} \cdot \Phi^l$	$= 0$	on $\Gamma_p^N \times (0, T]$,
$\mathbf{n} \cdot \Phi^+$	$= 0$	on $\Gamma_p^N \times (0, T]$,
$\mathbf{n} \cdot \Phi^-$	$= 0$	on $\Gamma_p^N \times (0, T]$.

(6.10)

7. CONCLUSION

In this article the swelling of charged porous media, like hydrated tissues is modelled by means of mixture theory. Considering four component for the mixture, solid, fluid, cation and anion we derived a set of balance equations for each component and for the mixture. The Lagrangian form of second law of thermodynamics complete the set of equations by means of constitutive equations. The equations are rewritten in Lagrangian description. Such a description is useful in computer-aided solutions. Finally the boundary conditions are given for this model.

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