Work and electrochemical potentials

$$d\underline{E} = \underbrace{\underset{\sim}{T} : d\underset{\sim}{E}}_{\text{mechanical part}} + \underbrace{\sum_{k,K} \mu^{ec}_{kK}\, dm^{kK}}_{\text{electrchemical part}}$$

$\underline{E}$: free energy per unit volume in the undeformed (reference, initial) configuration

$\underset{\sim}{T}$: ~~to~~tal stress tensor

$\underset{\sim}{E}$: strain tensor (2nd order)

k: individual species in phase K

ec: electrochemical potentian

m^{kK}: mass produced due to electrochemical effects (e.g. chemical reactions)

μ^{ec}_{kK}: electrochemical potential of species k in the phase K.

Formula for the electrochemical potential for compressible constituents

$$g^{ec}_{kK} = \hat{m}_k \mu^{ec}_{kK} = \underbrace{\int \hat{v}_k\, dp_{kK}}_{\text{"mechanical part"}} + \underbrace{RT\,\mathrm{Ln}\, x_{kK}}_{\text{chemical part}} + \underbrace{\zeta_k F \phi_K}_{\text{electrical part}}$$

$\hat{m}_k$, $\hat{v}_k$: molar mass and molar volume

p_{kK}: internal pressure

R: universal gas constant

T: absolute temperature

Ln: natural logarithm

x_{kK}: concentration (in moles) of species k in phase K, in the porous medium

ζ_k: valences of species k

F: Faraday equivalent charge

ϕ_K: electrical potential in phase K.

For incompressible costituents, we write

$$g^{ec}_{kK} = \hat{v}_k p_{kK} + RT\,\mathrm{Ln}\, x_{kK} + \zeta_k F \phi_K$$

Another way to write the energy equation

$$d\underline{E} = \underset{\sim}{T} : d\underset{\sim}{E} + \sum_{K=I,E} \sum_{(i,n)\in(K_{in},K_{ne})} \mu_{nK}\, dm^{iK}$$

$K_{in} = \{w, Na, Ca\}$ independent variables $K_{ne} = \{w, s_1 = NaCl, s_2 = CaCl_2\}$ ne: neutral elements

Another way to write the energy equation

$$d\underline{W} = d\underline{E} - d\underline{E}_I = \underset{\sim}{T} : d\underset{\sim}{E} + \sum_{(i,n)\in(E_{in},E_{ne})} \mu_{nE}\, dm^{iE} + p_I\, dv^I + \mu_{adh}\, dm^{wI}$$

$\underline{W}$: chemo elastic energy without the energy of the intrafibrillar phase ($d\underline{E}_I$)

p_I: intrinsic pressure in the intrafibrillar phase

μ_{adh}: potential to extract water from the intrafibrillar phase

We end up to the equation

$$d\underline{W} = \overline{\underset{\sim}{T}} : d\underset{\sim}{E} + \sum \overline{\mu}_n\, dm^{iE} + \mu_{adh}\, dm^{wI}$$

We obtain the dependent variables, via the differentiation

$$\underset{\sim}{S} = \frac{\partial \underline{W}}{\partial \underset{\sim}{\mathcal{E}}}$$

$\underset{\sim}{S}$: generalised stress tensor

$\underset{\sim}{\mathcal{E}}$: generalised strain tensor

More explicitly, we can write

$$\overline{\underset{\sim}{T}} = \frac{\partial \underline{W}}{\partial \underset{\sim}{E}}, \quad \overline{\mu}_{nE} = \frac{\partial \underline{W}}{\partial m^{iE}}, \quad \mu_{adh} = \frac{\partial \underline{W}}{\partial m^{wI}}$$

$\overline{\underset{\sim}{T}}$: shifted stress tensor

So

$$\underset{\sim}{S} = \begin{bmatrix} \overline{T} \\ \overline{\mu}_{wE} \\ \overline{\mu}_{NaE} \\ \overline{\mu}_{CaE} \\ \mu_{adh} \end{bmatrix} = \text{dependent variables (generalised stresses)}$$

The set of independent variables ("strains")

$$\underset{\sim}{\xi} = \begin{bmatrix} \underset{\sim}{E} \\ n^{wE} \\ n^{NaE} \\ n^{CaE} \\ n^{wI} \end{bmatrix}$$

In the governing equation we may have transport phenomena like diffusion or convection.

Set of species that we talk about

set	Species	Property
E	w, PG, Na, Ca, Cl	EF compartment
E_{ions}	Na, Cl, Ca	EF ions
E_{mo}	$E - \{PG\}$	EF mobile species
I_{in}	w, Na, Ca	Independent IF species
I_{ne}	$\{w\} \cup \{I_{salts}\}$	Neutral IF species
I_{salts}	$s_1 = NaCl, s_2 = CaCl_2$	IF salts

Balance equations which we have to solve

Momentum equation: $\operatorname{div} \underset{\sim}{\sigma} = \underset{\sim}{0}$

Incompressibility condition: $\operatorname{div} \vec{v}_s + \operatorname{div} \vec{J}_E = 0$

$\vec{J}_E$: flux of species in and out of the extrafibrillar (E) phase

Alternatively the incompressibility condition can be written as

$$\frac{1}{\det \underset{\sim}{F}} \frac{d v^{kE}}{dt} + \frac{1}{\det \underset{\sim}{F}} \frac{d v^{kI}}{dt} + \operatorname{div} \vec{J}_{kE} = 0$$

For the formation of chloride ions, in the intrafibrilla phase, we can write

$$\frac{1}{\det \underset{\sim}{F}} \frac{d n^{iI}}{dt} - O_i = 0$$

where O_i is a constitutive function for generating the species