The generalised strain components of $\underset{\sim}{\varepsilon}$ and the generalised shifted stress components of $\underset{\sim}{\Sigma}$, are

$$\underset{\sim}{\Sigma} = \begin{bmatrix} \underset{\sim}{\bar{T}} \\ \bar{\mu}_{wE} \\ \bar{\mu}_{NaE} \\ \bar{\mu}_{CaE} \\ \mu_{adh} \end{bmatrix} \begin{array}{c} \leftarrow \text{mechanics} \rightarrow \\ \leftarrow \text{hydro}\cancel{\text{chemo}}\text{mechanical coupling} \rightarrow \\ \leftarrow \text{chemomechanical coupling} \rightarrow \\ \leftarrow \quad \text{''} \quad \text{''} \quad \rightarrow \\ \leftarrow \text{adhesion coupling} \rightarrow \end{array} \underset{\sim}{\varepsilon} = \begin{bmatrix} \underset{\sim}{E} \\ m^{wE} \\ m^{NaE} \\ m^{CaE} \\ m^{wI} \end{bmatrix}$$

One possible partition of the energy $\underline{W}$, is an additive one like

$$\underline{W} = \underline{W}_{ch-mech} + \underline{W}_{ch} + \underline{W}_{ef}$$

where

$\underline{W}_{ch-mech}$: is a chemomechanical part

$\underline{W}_{ch}$: is a purely chemical part

W_{ef}: ~~is~~ a term associated to the enthalpies of formation of species

$$W_{ch} = \frac{RT}{V_0} \sum_{k \in E} N_{kE} \operatorname{Ln} N_{kE} - \frac{RT}{V_0} \Big(\sum_{k \in E} N_{kE}\Big) \operatorname{Ln}\Big(\sum_{\ell \in E} N_{\ell E}\Big)$$

$$= W_{ch}\big(N_{kE}, \underline{k \in E} - \{PG\}\big)$$

$$W_{ch-mech}(\underset{\sim}{\varepsilon}) = \underbrace{-p_{ch}(\underset{\sim}{\varepsilon})\,\varepsilon_{ch}}_{\text{coupled term}} + \underbrace{\underline{W}_{mech}(\underset{\sim}{E})}_{\text{purely mechanical term}} + \underbrace{\int_0^{m^{wI}} p_{adh}(m) \frac{dm}{\rho_w}}_{\text{purely chemical term}}$$

The coupled term gives rise to a a chemical stress

$$\underset{\sim}{T}^{ch} = -\left(p_{ch} + \varepsilon_{ch}\frac{\partial p_{ch}}{\partial \varepsilon_{ch}}\right)(\det \underset{\sim}{F})\underset{\sim}{F}^{-1}\cdot\underset{\sim}{F}^{-T}$$

The mechanical stress is

$$\underset{\sim}{T}^{mech} = \underset{\sim}{T}^{gs} + \underset{\sim}{T}^{c} = \frac{\partial \underline{W}_{mech}(\underset{\sim}{E})}{\partial \underset{\sim}{E}}$$

gs: ground substance (everything in the cartilage, the collagen fibers excluded)

c: collagen fibers

$$\varepsilon_{ch} = \det \underset{\sim}{F} - 1$$

We can write the mechanical constitutive equations via the relation

$$\underbrace{\underset{\sim}{T}}_{\text{overall stress}} + \Big(\underbrace{p_I}_{\substack{\text{incompressibility condition}\\\text{term which leads}\\\text{to the shifted stress}}} + \underbrace{p_{ch} + \varepsilon_{ch}\frac{\partial p_{ch}}{\partial \varepsilon_{ch}}}_{\substack{\text{chemical stress}\\\text{contribution}}}\Big)\det \underset{\sim}{F}\,\underset{\sim}{F}^{-1}\cdot\underset{\sim}{F}^{-T} = \underset{\sim}{T}^{gs} + \underset{\sim}{T}^{c} = \underset{\sim}{T}^{mech}$$

The $\underline{W}_{ef}$ term can be written as

$$\underline{W}_{ef}\left(m^{iE}, i \in E_{in}\right) = \frac{P_{fw}}{\rho_w}m^{wE} + \frac{P_{fs_1}}{\rho_{s_1}}m^{NaE} + \frac{P_{fs_2}}{\rho_{s_2}}m^{CaE}$$

in: independent species (w, Na, Ca)

s_1, s_2: salts $NaCl$ (s_1), $CaCl$ (s_2)

P_f: are refferred as pressures of formation of w, $NaCl$, $CaCl$.

Fluxes due to diffusion, transport, convection are used in the field equations, mainly the expression of conservation of mass. They include:

1) Darcy's law: $\vec{J}_H = -K_H \vec{\nabla} h$

J_H: flux of fluind relatve to the solid skeleton

K_H: hydraulic conductivity

h: hydraulic head (height difference)

2) Fick's law: $\vec{J}_s^d = -D_s \vec{\nabla} c$

s: solute D_s: diffusion coefficient

d: diffusion c: concentration of solute

3) Ohm's law: $\vec{I}_e = -\sigma_e \vec{\nabla} \phi$

$\vec{I}_e$: electrical current density

σ_e: electrical conductivity

ϕ: electrical potential

4) Fourier's law: $\vec{Q} = -k_T \vec{\nabla} T$

$\vec{Q}$: thermal flux

k_T: thermal conductivity

T: temperature

We may have coupled flow phenomena written in the form of

$$\vec{j} = -[K]\vec{f}$$

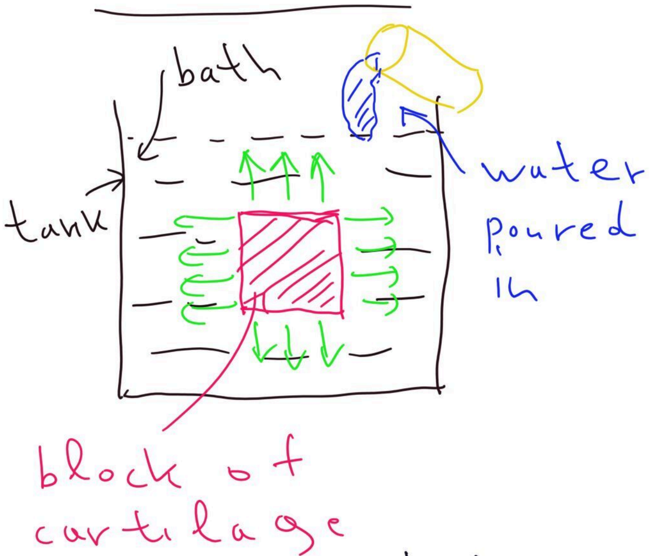
$$j_i = -K_{il} f_l$$

For example, we may have

$$\vec{j} = \begin{bmatrix} \vec{J}_{wE} \\ \vec{J}_{NaE} \\ \vec{J}_{caE} \\ \vec{J}_{clE} \end{bmatrix} \qquad \vec{f} = \begin{bmatrix} \rho_w \vec{\nabla} \mu_{wE} \\ \rho_{Na} \vec{\nabla} \mu^{ec}_{NaE} \\ \rho_{ca} \vec{\nabla} \mu^{ec}_{ca} E \\ \rho_{cl} \nabla \mu^{ec}_{clE} \end{bmatrix}$$

$$[K] = \begin{bmatrix} K_{ww} & K_{wNa} & K_{wCa} & K_{wcl} \\ K_{Naw} & K_{NaNa} & K_{NaCa} & K_{Nacl} \\ K_{Caw} & K_{CaNa} & K_{CaCa} & K_{Cacl} \\ K_{clw} & K_{clNa} & K_{clCa} & K_{clcl} \end{bmatrix}$$

<u>Experiment on cartilage with varying PH (due to varying water content</u>

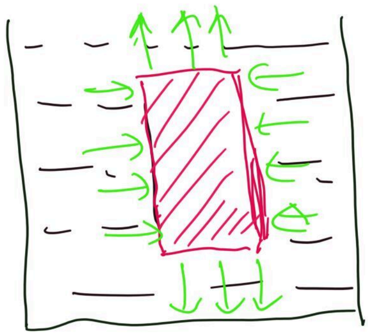


Free expansion in all directions, due to the reduction of the concentration of Na. The repulsive forces between the PG's become dominant.

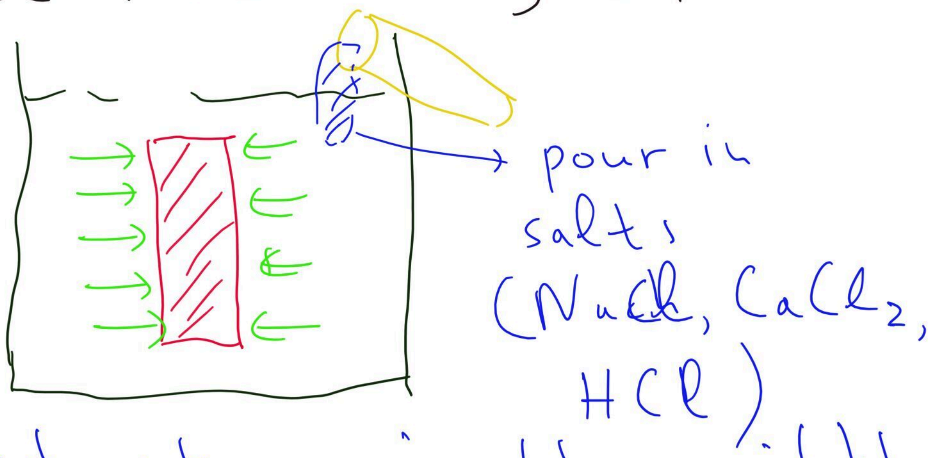
The bath contains initially high concentration of Na

We have the so called free swelling (no forces are applied).

Next, we apply uniaxial tension along the vertical direction, keeping the concentration of the bath, fixed



Next, we increase the concentration of salt, at fixed height.



We see reduction in the width due the reduction of the repulsive forces of the PG's, due to the increase of cation's (Na^+, Ca^{++}, H^+) concentration.