Effect of pH on mechanical properties and transport of articular cartilage.

pH (potential of hydrogen), or H^+ or H_3O^+ may alter the charge in the porous medium. As a consequence collagen may be changed. Also we may have chemical reaction and binding of ions to the proteoglycans. The chemical and electrical effect is obvious in the mechanical properties and transport phenomena in the medium. The model of the medium (articular cartilage) changes. Observations of experiments have proved that effect.

Phases of the model

S (solid) = {c} c: collagen

extra now

I (intrafibrular fluid): $I = \{w, Na, Ca, Cl, H, OH\}$

E (extrafibrular phase of fluid): $E = I + \{PG\}$

E.g. the effective molar fraction in the medium ~~extrafibrular phase~~ will include the quantity

$$\zeta_c \frac{N_c}{N}$$

N_c: number of moles of collagen

N: total number of moles

ζ_c: electric valence

This is plus to the $\zeta_{PG} \frac{N_{PG}}{N}$ which refers to the proteoglycans.

For a concentration of an l (index) element in the extrafibrular phase, we will have

$$C_{lE} = \frac{N_{lE}}{V_{E_0}} \frac{n_0^E}{n_0^E + \det \underset{\sim}{F} - 1}$$

n_0^E: porosity of E wrt the undeformed volume of the whole medium.

V_{E_0}: volume undeformed of phase E

$\underset{\sim}{F}$: deformation gradient tensor

C_{lE}: molar consentration per unit deformed volume of the E phase.

Incremental work done on the medium

$$\delta \underline{W} = \underset{\sim}{T} : \underset{\sim}{E} + \sum_{K, l \in K} g_{lK}^{ec} \delta N_{eK}$$

$$g_{eK}^{ec} = \underbrace{\hat{v}_e P_{eK}}_{\substack{\text{intrinsic} \\ \text{pressure} \\ \text{due to} \\ \text{the electro-} \\ \text{chemical} \\ \text{potential}}} + \underbrace{RT \operatorname{Ln} x_{eK}}_{\substack{\text{chemical} \\ \text{contribution}}} + \underbrace{\zeta_e F \phi_K}_{\substack{\text{electrical} \\ \text{contribution}}}$$

Chemical affinity is a form of chemical potentian related the the creation of mass due chemical reaction. It is denoted with the letter G (calligraphic). For the creation of H+ we have the expression (calligraphic)

$$\mathcal{G} = RT \operatorname{Ln} \frac{C_S}{C_{SH}} \frac{C_{HE}}{10^{-PK}}$$

Generalised diffusion (plus transport due to applied forces)

Flows — Gradients (vectorial elements)

$$\vec{J} = \begin{bmatrix} J_{wE} \\ J^{d}_{KE} \\ J^{d}_{ClE} \\ J^{d}_{HE} \\ J^{d}_{OHE} \\ I_{eE} \end{bmatrix}, \quad \vec{F} = \begin{bmatrix} F_{E} \\ F^{d}_{KE} \\ F^{d}_{ClE} \\ F^{d}_{HE} \\ F^{d}_{OHE} \\ F_{eE} \end{bmatrix} = \begin{bmatrix} \vec{\nabla} p_{w} \\ \frac{RT}{\hat{v}_K} \nabla \ln x_{KE} \\ \frac{RT}{\hat{v}_{Cl}} \nabla \ln x_{ClE} \\ \vdots \\ \vec{\nabla} \phi_{E} \end{bmatrix} - \begin{bmatrix} \rho^{E}/n^{E}\, \vec{g} \\ \left(\rho_K - \frac{\rho^{E}}{n^{E}}\right)\vec{g} \\ \left(\rho_{Cl} - \frac{\rho^{E}}{n^{E}}\right)\vec{g} \\ \vdots \\ 0 \end{bmatrix}$$

d upper index: for diffusive (purely) phenomena

General diffusion law

$$\vec{J} = -\underset{\sim}{K}\, \vec{F}$$

$$\underset{\sim}{K} = \begin{bmatrix} K_{EE} & & & & & K_{e} \\ & K^{d}_{KK} & & & & K^{d}_{Ke} \\ & & K^{d}_{ClCl} & & & K^{d}_{Cle} \\ & & & K^{d}_{HH} & & K^{d}_{He} \\ & & & & K^{d}_{OHOH} & K^{d}_{OHe} \\ K_{e} & K^{d}_{eK} & K^{d}_{eCl} & K^{d}_{eH} & K^{d}_{eOH} & \sigma_{e} \end{bmatrix}$$

Arrow head like diffusion matrix.

Constitutive modelling

$$\delta \underline{W} = \underbrace{\underset{\sim}{T} : \underset{\sim}{E}}_{\text{mechanical contribution}} + \underbrace{\sum_{l \in E_{mo}} g_{lE}\, \delta N^{*}_{lE}}_{\text{transport or diffusion contribution to the change of mass}} + \underbrace{\sum_{j \in [1,4] \cup [1']} G_j\, \delta N_{xE(j)}}_{\text{chemical reaction contribution to the change of mass}} + p_E\, \delta \underbrace{I_{inc}}_{=0 \text{ incompressibility}} + \phi_E\, \delta \underbrace{I_{cE}}_{=0 \text{ electroneutrality}}$$

Independent variables: $\underset{\sim}{E}$, Sets of mole contents $E_{mo} \cup E_{rea}$ (mobile + reactive), p_E, ϕ_E

Dependent variables: $\bar{\underset{\sim}{T}}$ (shifted stress)

$$\bar{\underset{\sim}{T}} = \underset{\sim}{T} + p_E \det \underset{\sim}{F}\, \underset{\sim}{F}^{-1} \cdot \underset{\sim}{F}^{-T}, \quad \bar{T} = \frac{\partial \underline{W}}{\partial \underset{\sim}{E}}$$

$$\bar{g}^{ec}_{lE} = \frac{\partial \underline{W}}{\partial N^{*}_{lE}} \quad \text{(electrochemical potentials)}$$

$$G_j = \frac{\partial \underline{W}}{\partial N_{xE(j)}} \quad \text{(reaction potentials)}$$

$$I_{inc} = \frac{\partial \underline{W}}{\partial p_E} = 0 \quad \text{(incompressibility measure)}$$

$$I_{cE} = \frac{\partial \underline{W}}{\partial \phi_E} = 0 \quad \text{(electroneutrality measure)}$$

We wrote the work conjugate pairs.

Chemical effect on mechanical activation of collagen fibers

$\vec{m}_c$: unit vector along a fiber direction

$\underset{\sim}{M}_c = \vec{m}_c \otimes \vec{m}_c$

A measure of the elongation of ~~a~~ fiber is

$$L = \frac{1}{2} \langle \underset{\sim}{C} : \underset{\sim}{M}_c - 1 \rangle = \langle \underset{\sim}{E} : \underset{\sim}{M}_c \rangle$$

$$\geqslant 0 \qquad\qquad \geqslant 0$$

Expression of the strain energy density of ~~a~~ single fiber

$\underline{w}_c = \frac{K_c}{2k_c}\left[e^{k_c L^2} - 1\right]$

$\frac{\partial \underline{w}_c}{\partial \underset{\sim}{E}}$ = stress

$\frac{\partial \underline{w}_c}{\partial \underset{\sim}{E}\,\partial \underset{\sim}{E}}$ = stiffness

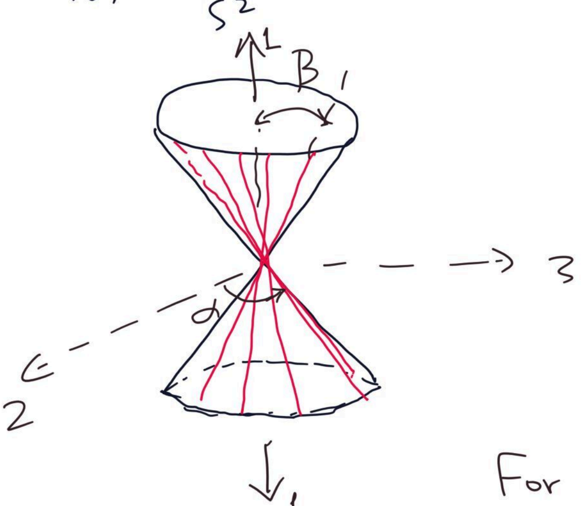
For a group (bundle) of collagen fibers

$\underline{W}^c(\underset{\sim}{E}) = n^c \int_{S^2} \underline{w}_c(L^2)\,\phi(\underline{\alpha}, \underline{\beta})\, dS$

Integration across the surface of the unit sphere

$\phi(\underline{\alpha}, \underline{\beta})$: distribution function of the fibers

$\underset{\sim}{\alpha}, \underset{\sim}{\beta}$: meridional and azimuthal angles of orientation of fibers



For axisymmetric distribution of fibers around axis 1, $\phi(\underline{\alpha}, \underline{\beta}) = \phi(\underline{\beta})$

Condition of posite stretch of the fibers

$\underset{\sim}{E} : \underline{M}_c \geq 0 \Rightarrow \cot^2 \underline{\beta} \geq \cot^2 \underline{\beta}_m = \frac{-E_{22}}{E_{11}}$

Angle range of activated fibers in tension

We have taken

$$\phi(\underline{\beta}) = \frac{\phi_0}{4\pi} + \frac{3}{4\pi}(1-\phi_0)(\cos\underline{\beta})^2$$

so

$$\underline{\beta} \in [0, \underline{\beta}_m] \cup [\pi - \beta_m, \pi]$$

for activated fibers.