

A Phenomenological Theory and Numerical Procedure for Chemo-Mechanical Coupling Behavior of Hydrogel

Q. S. Yang¹, B. S. Liu and L. T. Meng

Abstract: Coupling and interaction of multi-physical fields exist in hydrogel consisting of a fluid and a solid under external stimulus. In this paper, a phenomenological theory for chemo-mechanical coupling behavior and finite element formulation are developed, based on the thermodynamic laws. The free energy function is constructed and used to derive the constitutive equations and governing equations for a linear coupling system including a chemical effect. Equivalent integral forms of the governing equations and coupled finite element equations are obtained by a variational principle. Numerical examples demonstrate the interaction of chemical and mechanical effects of hydrogel under external force loadings and chemical stimuli. It is shown that the chemo-mechanical coupling behavior of hydrogel can be described by the theory and numerical method presented in this paper.

Keywords: hydrogel, chemo-mechanical coupling, constitutive equations, variational principle, coupled FE method

1 Introduction

Several materials used in industry and engineering, e.g. electrical active polymer, responsive hydrogel, make response to external environment stimuli. The chemical energy and mechanical energy exchange with each other in this process which leads to a chemo-mechanical coupling effect.

To characterize multi-field coupling behavior in a medium, many approaches have been proposed. In early works, the porous medium theory based on the Darcy's law was developed in Boer de (2003) to investigate the interaction of a solid and a liquid. In order to take into account a chemical effect which induces the mass diffusion or energy transformation in a medium, the liquid diffusion caused by electrochemistry effect as well as chemo-mechanical coupling effect was considered. Lai, Hou and Mow (1991) developed a triphasic model to describe the chem-

¹ Dept. of Engineering Mechanics, Beijing University of Technology, Beijing 100124, P. R. China. Corresponding author, Tel: +86 10 67396333, E-mail: qsyang@bjut.edu.cn

ical effect of ionic diffusion in articular cartilage. Gu, Lai and Mow (1997) presented an electro-chemo-mechanical coupling constitutive equation based on that triphasic model. Gajo, Loret and Hueckel (2002) presented the electro-chemo-mechanical coupling model of a porous medium by a conception of chemical consolidation. They developed electro-chemo-mechanical constitutive equations under elastic-plastic framework. Loret and Simoes (2004) developed a triphasic model of articular cartilage, taking into account balance equations of momentum and energy. And electro-chemo-mechanical coupling constitutive relation was discussed in their paper. Huyghe and Janssen (1997, 1999) presented an electro-chemo-thermo-mechanical coupling theory for an incompressible porous medium. In their model, each constituent satisfies the momentum equation, energy equation and entropy inequality. Frijns, Huyghe and Janssen (1997), Meerveld, Molenaar and Huyghe (2003) established equilibrium equations, diffusion equations and mass transfer equations using porous medium theory developed in Boer de. Wallmersperger, Kroplin and Gulch (2004) presented chemo-electro-mechanical coupling governing equations. These formulations consisted of a diffusion equation for describing the chemical field, a Poisson equation for the electric field and an equilibrium equation for mechanical field. An ionic concentration is considered as an independent variable in mechanical equations through Donnan's osmotic pressure [Qin and Yang (2008)]. De and Aluru (2004), De, Aluru and Johnson (2002) developed steady-state and instantaneous governing equations of hydrogels. Nernst-Planck's flux equation was applied to describe the transfer of ions. Then chemo-electro-mechanical coupling equations were solved using finite element method. Li, Ng and Yew (2005), Li, Yew and Lam (2004) presented the governing equation of chemo-electro-mechanical model for the finite deformation case. Lin and Yang (2008) introduced the pressure gradient into chemical diffusion in order to describe the chemo-mechanical coupling behavior of a hydrogel. Moreover, the diffusion phenomena can be found in alternative porous media, for instance, plant tissue [Mebatsion, Verboven, Jancsó, et al (2008)] and soft clay [Selvadurai, Ghiabi, (2008)]. An iterative homogenization approach is proposed in order to predict the nonlinear hydro-mechanical behaviour of porous media [Smaoui, Ben Hamida, Djeran-Maigre, et al (2006)].

In this paper constitutive equations and governing equations of the chemo-mechanical coupling are developed based on the definition of chemical potential and the basic laws of thermodynamics. The functional of chemo-mechanical coupling system is established in terms of free energy density, kinetic energy density and diffusion energy density. The equivalent integral form and finite element formulation of chemo-mechanical governing equations are obtained through discretization and variational methods [Qin and Yang (2008)]. The deformation and concentration dis-

tribution of the hydrogel under mechanical and chemical loading are got through a numerical examples.

2 Chemo-mechanical coupling equations

A chemo-mechanical coupling problem involves an interaction between ionic diffusion and mechanical field. When a hydrogel is bathed in a solution or subjected to a mechanical load, the change of the ionic concentration in hydrogel causes the swelling or shrinking of the medium.

A chemo-mechanical coupling constitutive equation would be established here. The elastic energy of the hydrogel can be written in the form[Gajo, Loret and Hueckel (2002)]

$$dW' = \sigma_{ij}d\varepsilon_{ij} \quad (1)$$

Where σ_{ij} is stress, ε_{ij} denotes strain. In this formulation Einstein summation convention is used, namely it implies that we are summing over all of its possible values when an index variable appears twice in a single term. When a porous medium under consideration, such as a hydrogel, has more than one constituent, the property of this porous medium is a function of thermodynamical variables, e.g. the mole number, pressure, temperature and entropy. The chemical potential is defined by [Levine (2002)]

$$\mu^i = \frac{\partial U}{\partial \bar{c}^i} \quad (2)$$

For the deformation of the hydrogel, it is an isochoric process, so the change of volume is ignored in this paper. The contribution of a chemical potential to internal energy is written in this form,

$$dW'' = \sum_{i=1} \mu^i d\bar{c}^i \quad (3)$$

where \bar{c}^i denotes the concentration of the constituent i . For a reversible process the second law of thermodynamics is $dQ = TdS$. Because the electrostatic field of the constituents is ignored as the electrostatic effect is relating small, the differential form of the total internal energy which is composed of the elastic energy, the chemical energy and thermal energy, is formulated as[Yang and Liu (2008)]

$$dU = TdS + \sigma_{ij}d\varepsilon_{ij} + \sum_{i=1} \mu^i d\bar{c}^i \quad (4)$$

Thus the Helmholtz free energy is defined by[Yang and Liu (2008)]

$$A = U - TS \quad (5)$$

For a reversible process, the incremental form of Helmholtz free energy can be obtained from Eq. (5).

$$\begin{aligned} dA &= dU - TdS - SdT \\ &= -SdT + \sigma_{ij}d\epsilon_{ij} + \sum_{i=1} \mu^i d\bar{c}^i \end{aligned} \quad (6)$$

When an infinitesimal increments dT , $d\epsilon_{ij}$ and $d\bar{c}^i$ are defined in balance state $T = T_0$, $\epsilon_{ij} = 0$, $\bar{c}^i = c_0^i$, the Helmholtz free energy is expanded by Taylor series in which dT , $d\epsilon_{ij}$ and $d\bar{c}^i$ are adopted as independent variables[Yang and Liu (2008)],

$$A \approx A_0 + \left(\frac{\partial A}{\partial T}\right) dT + \left(\frac{\partial A}{\partial \epsilon_{ij}}\right) d\epsilon_{ij} + \sum_{i=1} \left(\frac{\partial A}{\partial \bar{c}^i}\right) d\bar{c}^i \quad (7)$$

It is assumed that the entropy, the stress and the chemical potential in the balance state are zero, so we have

$$\begin{aligned} \left. \frac{\partial A}{\partial T} \right|_{\substack{T=T_0 \\ \epsilon_{ij}=0 \\ \bar{c}^i=\bar{c}_0^i}} &= -S^0 = 0 \\ \left. \frac{\partial A}{\partial \epsilon_{ij}} \right|_{\substack{T=T_0 \\ \epsilon_{ij}=0 \\ \bar{c}^i=\bar{c}_0^i}} &= \sigma_{ij}^0 = 0 \\ \left. \frac{\partial A}{\partial \bar{c}^i} \right|_{\substack{T=T_0 \\ \epsilon_{ij}=0 \\ \bar{c}^i=\bar{c}_0^i}} &= \mu_0^i = 0 \end{aligned} \quad (8)$$

With Eq. (7), the Eq. (8) can be expressed as

$$-dS = \left(\frac{\partial^2 A}{\partial T^2}\right) dT + \left(\frac{\partial^2 A}{\partial T \partial \epsilon_{ij}}\right) d\epsilon_{ij} + \sum_{i=1} \left(\frac{\partial^2 A}{\partial T \partial \bar{c}^i}\right) d\bar{c}^i \quad (9)$$

$$d\sigma_{ij} = \left(\frac{\partial^2 A}{\partial T \partial \epsilon_{ij}}\right) dT + \left(\frac{\partial^2 A}{\partial \epsilon_{ij} \partial \epsilon_{kl}}\right) d\epsilon_{kl} + \sum_{n=1} \left(\frac{\partial^2 A}{\partial \epsilon_{ij} \partial \bar{c}^n}\right) d\bar{c}^n \quad (10)$$

$$d\mu^m = \left(\frac{\partial^2 A}{\partial T \partial \bar{c}^m} \right) dT + \left(\frac{\partial^2 A}{\partial \varepsilon_{ij} \partial \bar{c}^m} \right) d\varepsilon_{ij} + \sum_{n=1} \left(\frac{\partial^2 A}{\partial \bar{c}^m \partial \bar{c}^n} \right) d\bar{c}^n \quad (11)$$

The above thermo-chemo-mechanical coupled constitutive equations are suitable to a linear and nonlinear coupling system while the variables in the brackets are material parameters.

Considering an isothermal process, namely the temperature increment $dT = 0$, constitutive equations for a linear chemo-mechanical coupled system can be obtained

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} + \sum_{m=1} H_{ij}^m c^m \quad (12)$$

$$\mu^n = H_{kl}^n \varepsilon_{kl} + \sum_{m=1} s_n^m c^m \quad (13)$$

where $C_{ijkl} = \frac{\partial^2 A}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}}$ is elastic stiffness coefficient, $H_{ij}^n = \frac{\partial^2 A}{\partial \varepsilon_{ij} \partial \bar{c}^n}$ is chemo-mechanical coupling coefficient, $s_n^m = \frac{\partial^2 A}{\partial \bar{c}^m \partial \bar{c}^n}$ is chemical stiffness coefficient. $\bar{c}^i = c_0^i + c^i$, c^i being the increment of concentration. It is noted that \bar{c}^i is replaced by c^i in Eq. (13) and (14) because of the condition at balance state (equation (8)).

For the medium bathed in a solution, only one of ions plays a dominant role, Eq. (12) and (13) can be specified to this form,

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} + H_{ij} c \quad (14)$$

$$\mu = H_{kl} \varepsilon_{kl} + s c \quad (15)$$

In classical physical chemistry [Levine (2002)], the chemical potential is defined by $\mu = \mu_0 + RT \ln \frac{c_0 + c}{c_0}$, where c_0 is ionic concentration in a reference state, c is increment of the ionic concentration. The partial derivative of this chemical potential leads to $\frac{\partial \mu}{\partial c} = \frac{RT}{c_0 + c}$. For small change of the ionic concentration, we have $c_0 + c \approx c_0$. Thus the second Fick's law is expressed by

$$\dot{\mu} + \frac{RT}{c_0} J_{i,i} = 0 \quad (16)$$

where R is the universal gas constant, J_i is a flux defined by $J_i = -D_{ij} c_{,j}$, D_{ij} is a ionic diffusion coefficient. Eq. (16) is a differential equation in terms of the ionic concentration increment.

The equilibrium equation of a mechanical field is

$$\sigma_{ij,j} + f_i - \rho \ddot{u}_i = 0 \quad (17)$$

where σ_{ij} , u_j , ρ are stress, displacement and mass density, respectively. f_i is a external body force of the porous medium. Eq. (16) and Eq. (17) compose the governing equations of the present problem where the displacement u_i and concentration increment c are independent variables. The corresponding gradient equations of the mechanical and chemical fields are

$$\varepsilon_{ij} = \frac{1}{2}(u_{j,i} + u_{i,j}), \quad J_i = -D_{ij}c_{,j} \quad (18)$$

All equations of this chemo-mechanical coupling problem are composed of the constitutive equation (14) and (15), the divergence equations (16) and (17), and the gradient equation (18).

From Eqs. (14) to (18), basic equations of this chemo-mechanical coupling problem are obtained

$$\sigma_{ij,j} + RTc_{,i} + f_i - \rho\ddot{u}_i = 0 \quad (19)$$

$$c_0 \frac{\partial \varepsilon_v}{\partial t} + \frac{\partial c}{\partial t} - D_{ij}c_{,ij} = 0 \quad (20)$$

where ε_v is the volume strain of the medium. Eq. (19) is viewed as a mechanical equilibrium equation with the chemical effect and Eq. (20) is a continuity equation including a mechanical deformation. They are coupled with each other. We can solve these equations for the given initial-boundary condition by a finite element method.

3 Finite element formulations

The functional of the chemo-mechanical coupling system based on governing equations of a hydrogel is established by using the kinetic energy density, free energy density and diffusion energy density[Mindlin (1974)]. Then the equivalent integral weak form and the finite element formulation are obtained through the discretization of the equivalent integral equations.

Using energy principle, the functional of this chemo-mechanical coupling process is obtained

$$\pi = \int_V (\dot{K} + \dot{\phi} + F - f_i \dot{u}_i) dV - \int_S \left(\bar{t}_i \dot{u}_i - \frac{RT}{c_0} \bar{q}c \right) dS \quad (21)$$

where \bar{q} and \bar{t}_i is a concentration flux and a traction on the surface, respectively. The boundary conditions are in the forms $\sigma_{ij}n_j = \bar{t}_i$, $J_in_i = \bar{q}$. The physical meanings of every term in Eq. (21) are interpreted as follows: K is a kinetic energy density,

F is a chemical diffusion energy and ϕ is a generalized free energy density which satisfied the following conditions

$$\sigma_{ij} = \frac{\partial \phi}{\partial \varepsilon_{ij}}, \quad \mu = \frac{\partial \phi}{\partial c} \quad (22)$$

The second integration on the right hand side of Eq. (21) stands for the work done by the boundary force and the chemical transformation. Using variational principle for Eq. (21), the following formulation is obtained

$$\begin{aligned} \delta \pi &= \int_V (\delta \dot{K} + \delta \dot{\phi} + \delta F - f_i \delta \dot{u}_i) dV - \int_S \left(\bar{t}_i \delta \dot{u}_i - \frac{RT}{c_0} \bar{q} \delta c \right) dS \\ &= \int_V \left(\rho \ddot{u}_i \delta \dot{u}_i + \sigma_{ij} \delta \dot{\varepsilon}_{ij} + \dot{\mu} \delta c + \frac{RT}{c_0} D_{ijc,i} \delta c_{,j} - f_i \delta \dot{u}_i \right) dV \\ &\quad - \int_S \left(\bar{t}_i \delta \dot{u}_i - \frac{RT}{c_0} \bar{q} \delta c \right) dS \\ &= 0 \end{aligned} \quad (23)$$

Eq. (23) can be divided into two parts, namely $\delta \pi = \delta \pi_1 + \delta \pi_2$, and $\delta \pi_1$ only depends on δu_i and $\delta \pi_2$ only on δc . Because δu_i and δc are arbitrary, two equations can be obtained

$$\begin{aligned} \delta \pi_1 &= \int_V (\delta \dot{\varepsilon}_{ij} \sigma_{ij} - \delta \dot{u}_i f_i + \delta \dot{u}_i \rho \ddot{u}_i) dV - \int_S \delta \dot{u}_i \bar{t}_i dS \\ &= 0 \end{aligned} \quad (24)$$

$$\begin{aligned} \delta \pi_2 &= \int_V \left(\delta c \dot{\mu} + \frac{RT}{c_0} \delta c_{,i} D_{ijc,j} \right) dV + \int_S \left(\frac{RT}{c_0} \delta c \bar{q} \right) dS \\ &= 0 \end{aligned} \quad (25)$$

By Eq. (24) and (25), the basic equations and the boundary conditions of the chemo-mechanical system can be obtained [Qin and Yang (2008)]. Using the constitutive equation Eqs. (14) and (15) and the time integration from 0 to t , Eq. (24) and (25) are written as

$$\int_V (\delta \varepsilon_{ij} C_{ijkl} \varepsilon_{kl} + RT c \delta \varepsilon_v - \delta u_i f_i) dV - \int_{\Gamma_\sigma} \delta u_i \bar{t}_i dS = 0 \quad (26)$$

$$\int_V \left(c_0 \delta c \frac{\partial \varepsilon_v}{\partial t} + \delta c \frac{\partial c}{\partial t} - \delta c_{,i} D_{ijc,j} \right) dV + \int_{\Gamma_q} \delta c \bar{q} dS = 0 \quad (27)$$

These are the equivalent integral weak form of the chemo-mechanical coupling system. These equations will be used to generate finite element formulations.

The volume V is discretized into several finite domains V^e . The displacement and concentration of per element is defined by its corresponding values at nodes. \mathbf{N}_u and \mathbf{N}_c are shape functions of the displacement and concentration of the element and the interpolation forms are

$$\mathbf{d}_e^u = \mathbf{N}_u \mathbf{u}^e, \quad \mathbf{d}_e^c = \mathbf{N}_c \mathbf{c}^e \quad (28)$$

where $\mathbf{c}^e = (c_1 \ \cdots \ c_m)^T$ is a vector of nodal concentrations, $\mathbf{u}^e = (u_1 \ v_1 \ \cdots \ u_n \ v_n)^T$ is a vector of nodal displacements. The corresponding strain of an element is $\boldsymbol{\varepsilon}^e = \mathbf{B}_u \mathbf{u}^e$ and the volume part of the strain is $\boldsymbol{\varepsilon}_v^e = \mathbf{B}_v \mathbf{u}^e$. By substituting the interpolation function and the corresponding strain into Eqs. (26) and (27), we can obtain equations

$$\begin{aligned} & \sum_{e=1}^E \int_{V^e} \left(\delta \mathbf{u}^{eT} \mathbf{B}_u^T \mathbf{C}^e \mathbf{B}_u \mathbf{u}^e + \delta \mathbf{u}^{eT} \mathbf{B}_v^T R T \mathbf{N}_c \mathbf{c}^e - \delta \mathbf{u}^{eT} \mathbf{N}_u \mathbf{f} \right) dV \\ & - \sum_{e=1}^E \int_{\Gamma_\sigma^e} \delta \mathbf{u}^{eT} \mathbf{N}_u \mathbf{T} dS = 0 \end{aligned} \quad (29)$$

$$\begin{aligned} & \sum_{e=1}^E \int_{V^e} \left(c_0 \delta \mathbf{c}^{eT} \mathbf{N}_c^T \mathbf{B}_v \frac{\partial \mathbf{u}^e}{\partial t} + \delta \mathbf{c}^{eT} \mathbf{N}_c^T \mathbf{N}_c \frac{\partial \mathbf{c}^e}{\partial t} - \delta \mathbf{c}^{eT} \mathbf{B}_c^T \mathbf{K}_D^e \mathbf{B}_c \mathbf{c}^e \right) dV \\ & + \sum_{e=1}^E \int_{\Gamma_q^e} \delta \mathbf{c}^{eT} \mathbf{N}_c \bar{q} dS = 0 \end{aligned} \quad (30)$$

The vectors of the nodal displacements and concentrations are denoted by \mathbf{u} and \mathbf{c} respectively, the matrix forms of finite element equations are written as

$$\mathbf{K}_s \mathbf{u} + R T \mathbf{M} \mathbf{c} = \mathbf{F}_s \quad (31)$$

$$c_0 \mathbf{M}^T \frac{\partial \mathbf{u}}{\partial t} + \mathbf{X} \frac{\partial \mathbf{c}}{\partial t} + \mathbf{K}_c \mathbf{c} = \mathbf{F}_c \quad (32)$$

where \mathbf{K}_s and \mathbf{K}_c are the elastic stiffness matrix and the diffusion matrix, respectively,

$$\mathbf{K}_s = \sum_{e=1}^E \int_{V^e} \mathbf{B}_u^T \mathbf{C} \mathbf{B}_u dV \quad (33)$$

$$\mathbf{K}_c = - \sum_{e=1}^E \int_{V^e} \mathbf{B}_c^T \mathbf{D} \mathbf{B}_c dV$$

The mass transport matrix \mathbf{M} and the coupling coefficient matrix \mathbf{X} are

$$\mathbf{M} = \sum_{e=1}^E \int_{V^e} \mathbf{B}_v^T \mathbf{N}_c dV, \quad \mathbf{X} = \sum_{e=1}^E \int_{V^e} \mathbf{N}_c^T \mathbf{N}_c dV \quad (34)$$

On the right hand side of Eq. (31) and (32), \mathbf{F}_s and \mathbf{F}_c are a vector of equivalent nodal force and a vector of equivalent nodal flux, respectively,

$$\begin{aligned}\mathbf{F}_s &= \sum_{e=1}^E \int_{V^e} \mathbf{N}_u^T \mathbf{f} dV + \sum_{e=1}^E \int_{\Gamma_\sigma^e} \mathbf{N}_u^T \mathbf{t} dS \\ \mathbf{F}_c &= - \sum_{e=1}^E \int_{\Gamma_q^e} \mathbf{N}_c^T \bar{q} dS\end{aligned}\quad (35)$$

Eq. (31) and (32) are the finite element formulation including chemo-mechanical coupling effect. It can be discretized in the time domain using a linear difference

$$\frac{\partial \mathbf{u}}{\partial t} = \frac{\mathbf{u}_{n+1} - \mathbf{u}_n}{\Delta t}, \quad \frac{\partial \mathbf{c}}{\partial t} = \frac{\mathbf{c}_{n+1} - \mathbf{c}_n}{\Delta t}\quad (36)$$

and then

$$\begin{aligned}\mathbf{u} &= \theta \mathbf{u}_{n+1} + (1 - \theta) \mathbf{u}_n \\ \mathbf{c} &= \theta \mathbf{c}_{n+1} + (1 - \theta) \mathbf{c}_n\end{aligned}\quad (37)$$

where θ is a constant and $0 \leq \theta \leq 1$. Substituting Eq. (37) into Eq. (31) and (32) yields

$$\begin{aligned}& \begin{bmatrix} \theta \mathbf{K}_s & \theta R T \mathbf{M} \\ c_0 \mathbf{M}^T & \mathbf{X} + \theta \mathbf{K}_c \Delta t_n \end{bmatrix} \begin{Bmatrix} \mathbf{u}_{n+1} \\ \mathbf{c}_{n+1} \end{Bmatrix} \\ &= \begin{bmatrix} (\theta - 1) \mathbf{K}_s & (\theta - 1) R T \mathbf{M} \\ c_0 \mathbf{M}^T & -\mathbf{X} + (\theta - 1) \mathbf{K}_c \Delta t_n \end{bmatrix} \begin{Bmatrix} \mathbf{u}_n \\ \mathbf{c}_n \end{Bmatrix} + \begin{Bmatrix} \mathbf{F}_s \\ \Delta t_n \mathbf{F}_c \end{Bmatrix}\end{aligned}\quad (38)$$

In above equations, the stiffness matrixes are \mathbf{K}_s , \mathbf{K}_c , \mathbf{M} and \mathbf{X} . Solving of Eq. (28) can be implemented by extending the general finite element program.

4 Application examples

The chemo-chemical coupling behavior of a hydrogel plate under an external loading and a concentration stimulus is modeled and the deformation of the hydrogel plate is analyzed. The constants of the material involved in the hydrogel plate are shown in Tab. 1.

Example 1: A hydrogel plate with $22 \times 4 \text{mm}^2$ is considered to examine the swelling of the model, as shown in Figure 1. The bottom boundary of this plate is constrained, and the other boundaries are free. A uniform chemical load is applied on the boundaries of the hydrodel plate except the bottom line. The concentration

Table 1: Material constants

Young's modulus E	1.08MPa
Poisson's ratio ν	0.1
Diffusivity D^+	$4.9 \times 10^{-10} \text{m}^2/\text{s}$
Initial concentration c_0^+	$0.159 \text{kmol} / \text{m}^3$
Universal gas constant R	$8.314 \text{ J} / \text{mol} \cdot \text{K}$
Absolute temperature T	298 K

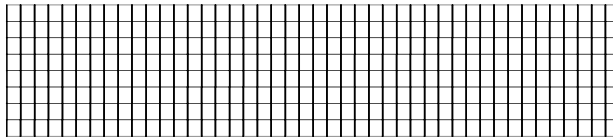


Figure 1: FE Mesh

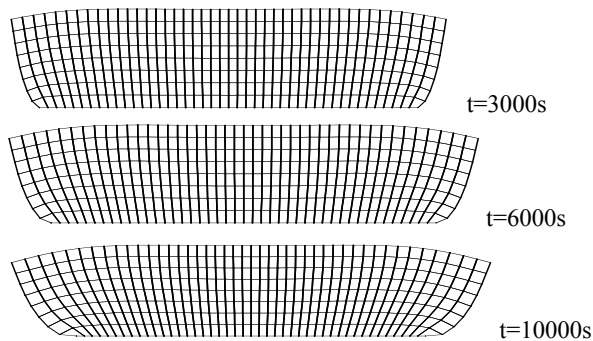


Figure 2: Swelling of hydrogel under chemical loading

of external solution is $0.159 \text{kmol} / \text{m}^3$. And this chemical load is applied on the boundaries with a concentration increment $0.02 \text{kmol} / \text{m}^3$ at each time step.

When the concentration of the hydrogel plate continuously increases on the boundary, the osmotic pressure induced by the concentration difference between the external solution and plate makes some small molecules to diffuse into the hydrogel plate. This leads to the swelling of the hydrogel plate, as shown in Figure 2. The swelling of the hydrogel plate develops with increase of the time.

From Figure 2 we can see that the hydrogel plate has a great deformation in left

and right ends, but small change at the center of the hydrogel plate. This indicates that the concentration diffusion is a process from the boundaries to the center of the hydrogel plate and can reach a new balance state.

Example 2: A swelling of a hydrogel plate with displacement constraints in left and right ends is studied, as shown in Figure 3. A chemical load is applied on bottom and top boundaries of the hydrogel plate, which leads to a symmetrical boundary condition. The swelling deformation and the contour of the displacement u_y are shown in Figures 4 and 5, respectively. It is shown that the swelling deformation of the hydrogel plate is symmetrical under present boundary conditions. Due to the displacement constraints on the left and right boundaries, there only exists swelling displacement in vertical direction.



Figure 3: Boundary conditions

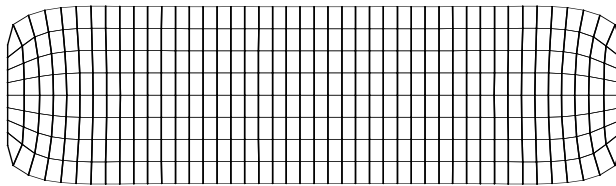


Figure 4: Swelling of plate under chemical loading

Example 3: A coupling behavior of a hydrogel plate under a traction loading is taken into account in this example, to verify the interaction of chemical and mechanical effect. The deformation and concentration distribution of the hydrogel plate subjected to a distributed loading are considered. The external load and constraint conditions are shown in Figure 6 where $q = 3.37\text{N} / \text{mm}$ is assumed.

Figure 7 illustrates the deformation of the plate under a traction loading. It can be found that the deformation of the plate with chemo-mechanical coupling effect is quite different from a pure elastic deformation. Here the deformation induces a concentration redistribution of ions. The deformation and the concentration distribution vary with time. Figure 8 shows the concentration contours at $t=100000\text{s}$

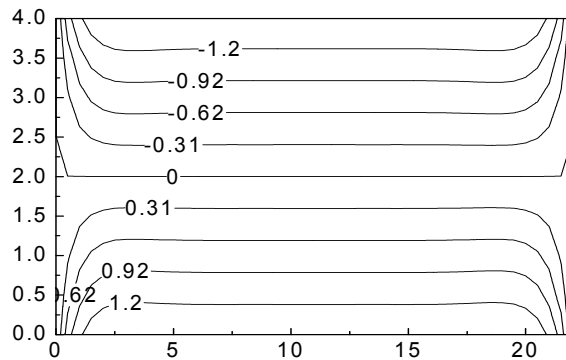
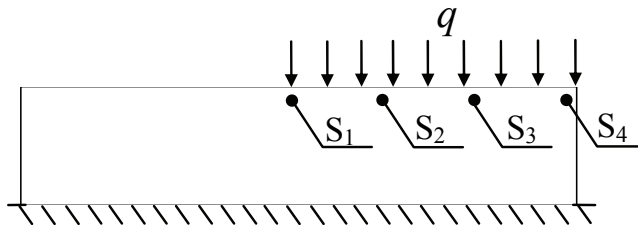
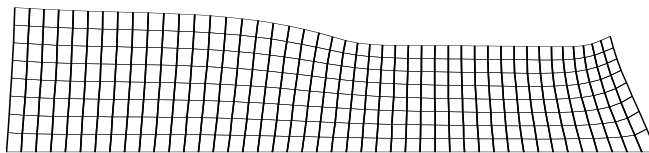
Figure 5: Contour of displacement u_y 

Figure 6: Distributed force and constraint condition

Figure 7: Deformation of coupling model under distributed force ($t=100000s$)

which stands for a near balance state. An inhomogeneous deformation and concentration distribution can be found in Figure 7 and Fig 8. The variation of the concentration versus time in different sample positions are shown in Figure 9. Although the inhomogeneity of concentration distribution leads to that concentration levels are different in the plate, a new balance state would be reached gradually with increase of time.

Example 4: A symmetric concentration load is considered here. The initial concentration in hydrogel is $0.159 \text{ kmol} / \text{m}^3$ and the concentration load in the left and

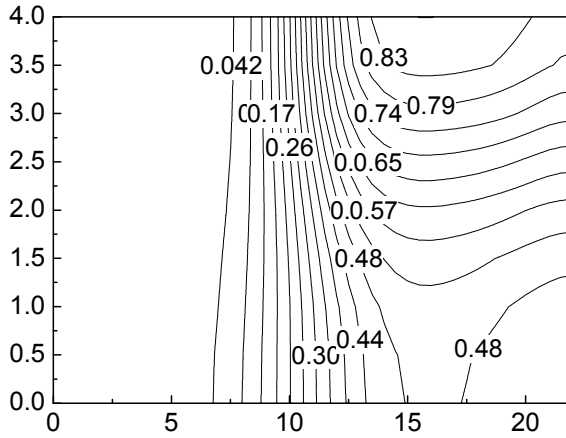


Figure 8: Contour of concentration under distributed force (t=100000s)

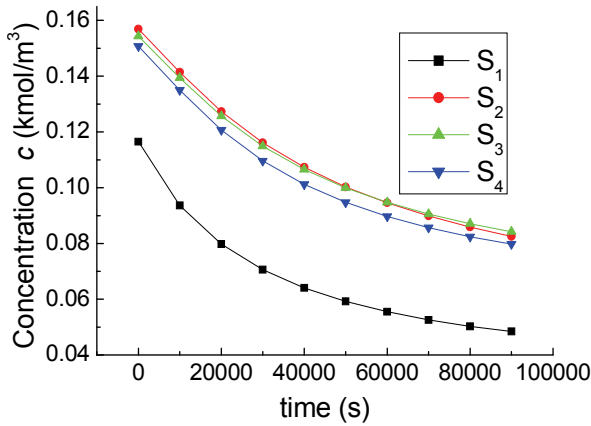


Figure 9: Concentration versus time under distributed force

right ends is $0.6\text{kmol} / \text{m}^3$ as shown in Figure 10. According to the numerical result, ions can diffuse from the right and left ends to the center. Finally the concentration of hydrogel in a balance state is $0.17\text{kmol} / \text{m}^3$. The ion diffusion and deformation contours of hydrogel are shown in Figure 11 and Figure 12. It is shown that the x-direction displacement of hydrogel is symmetrical in a balance state.

The time-varying concentration curves at the sample points are shown in Figure 13. The concentration at point S_1 , which is $0.6\text{kmol} / \text{m}^3$ in the initial state and higher



Figure 10: Boundary condition for concentration loading

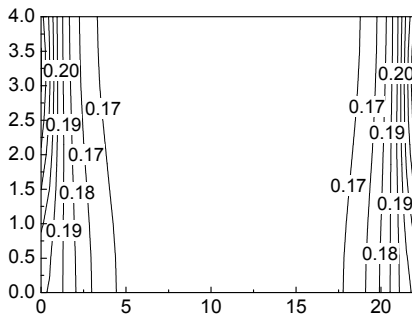


Figure 11: Contour for concentration diffusion (time=100000s)

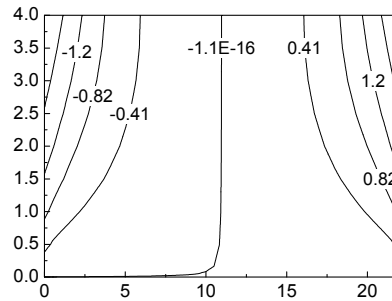


Figure 12: Contour of displacement u_x at a new balance state

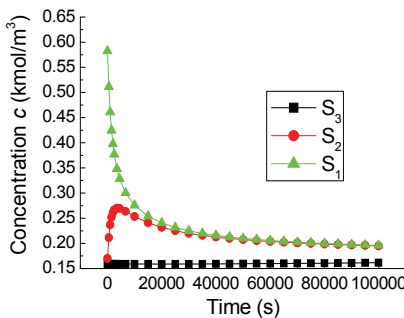


Figure 13: Concentration variation versus time

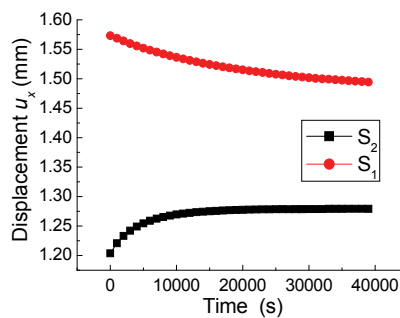


Figure 14: Variation of displacement u_x

than $0.17 \text{ kmol} / \text{m}^3$, gradually decreases to the concentration at the balance state. While the concentration at point S_2 increases to $0.275 \text{ kmol} / \text{m}^3$ at first and then decreases to $0.17 \text{ kmol} / \text{m}^3$. The concentration at point S_3 slowly increases from $0.159 \text{ kmol} / \text{m}^3$ up to the value at the balance state.

The deformation induced by an external chemical stimulus is shown in Figure 14 where curves of displacement at points S_1 and S_2 are plotted. We can see that the

displacement u_x at S_1 gradually decreases and the displacement u_x at S_2 increases with time. Then they tend to the balance state. It is shown that the mechanical energy and chemical energy exchange with each other in the chemo-mechanical coupling process.

5 Concluding remarks

The governing equations of this chemo-mechanical coupling problem have been established based on the thermodynamical laws. The equivalent integral form and finite element formulations of this chemo-mechanical coupling problem have been developed through a energy functional and variational principle. The physical meaning of the chemo-mechanical coupling problem has been interpreted as a energy transformation. The coupled stiffness matrix in present finite element method reflects the interactions of the chemical and mechanical system. The chemo-mechanical coupling behavior of a hydrogel under external loadings has been simulated by using the present finite element procedure. The numerical examples demonstrate that a mechanical load can induce redistribution of ionic concentration, while a chemical stimulus lead to swelling or shrinking of the hydrogel. The detailed discussions on the numerical results validate the rationality and effectiveness of the present theory and method. The experimental validation of the present results is expected.

Acknowledgement: The supports of the Natural Science Foundation of China under grant No 10872011 and Natural Science Foundation of Beijing under grant No 3092006 are gratefully acknowledged.

References

- Boerde, R.** (2003): Reflections on the Development of the Theory of Porous Media. *Appl. Mech. Rev.*, vol. 56, no.6, pp. 27-42.
- De, S. K.; Aluru, N. R.** (2004): A chemo-electro-mechanical mathematical model for simulation of pH sensitive hydrogels. *Mechanics of Materials*, vol. 36, pp. 395-410.
- De, S. K.; Aluru, N. R.; Johnson, B.** (2002): Equilibrium Swelling and Kinetics of pH-Responsive Hydrogels: Models, Experiments, and Simulations. *Journal of Micro-electro- mechanical systems*, vol.11, no.5, pp. 544-555.
- Frijns, A. J. H.; Huyghe, J. M.; Janssen, J. D.** (1997): A Validation of the Quadrasonic Mixture Theory for Intervertebral Disc Tissue. *Int J Engng Sci*, vol. 35, no. 15, pp. 1419-1429.
- Gajo, A.; Loret, B.; Hueckel, T.** (2002): Electro-Chemo- Mechanical Couplings

in Saturated Porous Medium: Elastic- Plastic Behaviour of Heteroionic Expansive Clays. *Int. J Solids Struct.*, vol. 39, pp. 4327-4362.

Gu, W. Y.; Lai, W. M.; Mow, V. C. (1997): A Triphasic Analysis of Negative Osmotic Flows Through Charged Hydrated Soft Tissues. *Journal of Biomechanics*, vol.30, no. 1, pp. 71-78.

Huyghe, J. M.; Janssen, J. D. (1997): Quadriphasic Mechanics of Swelling Incompressible Porous Medium. *Int J Engng Sci.*, vol. 35, no. 8, pp. 793-802.

Huyghe, J. M.; Janssen, J. D. (1999): Thermo-Chemo- Electro-Mechanical Formulation of Saturated Charged Porous Solids. *Transport in Porous Medium*, vol.34, pp. 129-141.

Lai, W. M.; Hou, J. S.; Mow, V. C. (1991): A Triphasic Theory for the Swelling and Deformation Behaviors of Articular Cartilage. *J Biomech Engng.*, vol. 113, pp. 245-258.

Levine, I. N. (2002): *Physical Chemistry, 5th edition*, McGraw Hill.

Li, H.; Ng, T. Y.; Yew, Y. K. (2005): Modeling and Simulation of the Swelling Behavior of pH- Stimulus- Responsive Hydrogels. *Biomacromolecule*, vol.6, pp. 109-120.

Li, H.; Yew, Y. K.; Lam, K. Y. (2004): Numerical Simulation of pH-stimuli Responsive, Hydrogel in Buffer Solutions. *Colloids and Surfaces A: Physicochem Eng. Aspects*, vol. 249, pp. 149-154.

Lin, L.; Yang, Q. S. (2008): The Basic Equations of Chemo-Mechanical Coupling and the Corresponding Numerical Analysis. *Acta Mechanica Solida*, vol. 29, no. 1, pp. 7-12.

Loret, B.; Simoes, F. M. F. (2004): Articular Cartilage with Intra- and Extrafibrillar Waters: A Chemo-Mechanical Model. *Mechanics of Materials*, vol. 36, pp. 515-541.

Mebatsion, H.K.; Verboven, P.; Jancsó, P. T.; et al (2008): Modeling 3D Fruit Tissue Microstructure Using a Novel Ellipsoid Tessellation Algorithm, *CMES: Computer Modeling in Engineering & Sciences* vol. 29, no. 3, pp. 137-149.

Meerveld, J. V.; Molenaar, M. M.; Huyghe, J. M. (2003): Analytical Solution of Compression, Free Swelling and Electrical Loading of Saturated Charged Porous Medium. *Transport in Porous Medium*, vol. 50, pp. 111-126.

Mindlin, R. D. (1974): Equations of High Frequency Vibrations of Thermopiezoelectric Crystal Plates. *Int J of Solids Struct.*, vol. 10, pp. 625-637.

Qin, Q. H.; Yang, Q. S. (2008): *Macro-Micro Theory on Multifield Coupling Behavior of Heterogeneous Materials*. Springer.

Selvadurai, A.P.S.; Ghiabi, H. (2008): Consolidation of a Soft Clay Composite: Experimental Results and Computational Estimates, *CMES: Computer Modeling in Engineering & Sciences* vol. 23, no. 1, pp.53-73.

Smaoui, S.; Ben Hamida, A.; Djeran-Maigre, I.; et al (2006): Micro-macro Approaches Coupled to An Iterative Process for Nonlinear Porous Media, *CMC: Computers, Materials, & Continua* vol. 4, no. 3, pp153-162.

Wallmersperger, T.; Kroplin, B.; Gulch R. W. (2004): Coupled Chemo-Electro-Mechanical Formulation for Ionic Polymer Gels–Numerical and Experimental Investigations. *Mechanics of Materials*, vol. 36, pp. 411-420.

Yang, Q. S.; Liu, B. S. (2008): Constitutive Law and FEM Equations of Chemo-mechanical Coupling. *Journal of Beijing university of technology*, vol. 34, pp.120-125.

