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Unsaturated Hydro-Mechanical-Chemical Constitutive Coupled Model Based on Mixture Coupling Theory: Hydration Swelling and Chemical Osmosis

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Abstract

Very low permeability soils and rocks may act as actual semi-permeable membranes and also have the potential to swell if they contain clay minerals. This study extends Mixture Coupling Theory for unsaturated, very low permeability swelling rock, based on non-equilibrium dynamics and Biot's elasticity, and develops new advanced coupled mathematical formulations, by including unsaturated chemical osmosis and hydration swelling. Helmholtz free energy has been used to derive the link between solid deformation and multiphase transport. Darcy's law has been extended and the influence of swelling on stress and strain has been included. The mathematical formulation shows that swelling capacity may have a strong influence on the deformation of host rock in the chemical osmosis process, which is demonstrated by a numerical simulation of two representative cases. Important engineering applications of this model and analysis are highlighted.

Keywords: Biot's theory; Mixture Coupling theory; non-equilibrium thermodynamics; osmotic flow; unsaturated

1: Introduction

Designs for the geological disposal of spent nuclear fuel and vitrified High Level Waste (HLW) in several European countries [e.g. [1, 2]]is based on a multi barrier concept to limit the migration of radionuclides to the biosphere. These barriers include: (1) the radioactive waste, including the uranium oxide fuel matrix or in the case of HLW a borosilicate glass; (2) metal containers, including a copper over pack [1];(3) a swelling clay buffer material that provides a hydraulic seal around the canister ; and (4) a suitable host rock a depth of typically 500 to 1,000 m which will isolate the waste from the biosphere. Where the host rock is comprised of low permeability clays [2] it will provide a further hydraulic barrier.

Clay hostrocks and clay (bentonite) buffer materials plays a key function of preventing egress of radionuclides. A key design criteria for the selection of potential materials for both the engineered and natural barriers for such waste disposal facilities is the achievement of a very low gas and hydraulic conductivity. A hydraulic conductivity $<10^{-10}$ m/s, often proposed for this purpose, may lead to chemical osmosis, in which the host rock and buffer clay may act as semi-permeable membranes for solute transport [3]. During groundwater resaturation through the host rock or buffer clay containing minerals, complex chemical reactions may occur which change the groundwater chemistry [4]. Where a semi-permeable membrane is developed chemical osmosis may induce water flow including changes in flow direction. Chemical osmosis may then significantly change the flow direction. Another important factor is that clay minerals (e.g. smectites) may swell in contact with groundwater, such that the combination of chemical osmosis and swelling of minerals may exert an important influence on the effective fluid permeability and contaminant flux within a barrier.

Some work has been published related to chemical osmosis around nuclear waste containers [5-7], and Darcy's Law has then been extended by including chemical osmosis for very low permeability rocks [8, 9]. Recently, Chen and Hicks (2013)[10] considered chemical osmosis in unsaturated conditions for I/LLW, due to H_2 that may be generated from the chemical reactions with the waste containers. However, further research is needed for unsaturated chemical osmosis in rocks which exhibit potential swelling properties according to their mineralogy and groundwater chemistry in contact with them.

There are two major approaches in modeling coupled fluids in deformable porous media: Mechanics approach and Mixture theory, as discussed by Chen[11]. The Mechanics approach is based on the classical consolidation theories of Terzaghi [12] and Biot [13, 14]. Work done in this approach in Geomechanics includes coupled hydro-mechanical models [15-19], and coupled thermo-hydro-mechanical-chemical models [20-22]. However, the Mechanics approach lacks systemic self development theory [23].

The rigorous theoretical framework of Mixture theory, first developed by Truesdell in 1957 and used for modelling of biological tissues, was most recently extended by Rajagopal et al. [24-28]. Rajagopal and Tao (1995, 2005) have also re-examined Biot's equations and placed them within the context of the theory of mixtures, concluding that Biot's approach can be obtained as a special case of Mixture theory [24, 29]. However, as Mixture theory maintains the individuality of the phases, it is very difficult to obtain information on the interaction between the phases. This has restrained the application of Mixture theory, as discussed by Rajagopal et al. (1986) [24, 25].

Mixture Coupling theory (formerly known as Modified Mixture Theory) is based on the

approach proposed by Heidug and Wong, which does not explicitly discriminate between solid and fluid phases, but views a fluid-infiltrated material as a single continuum. Chen et al. [10, 30-32] have continued extended Mixture Coupling theory to unsaturated, non-isothermal conditions, and compared this with the traditional Mixture theory and Mechanical approaches. In this paper, a new coupled formulation, including combined chemical osmosis and hydration swelling in unsaturated conditions, is developed by using Mixture Coupling theory. Helmholtz free energy is used to bridge external couplings (between the porous medium and fluid) and internal coupling (between different multiphase flows). Reflection and swelling coefficients, which are a measure of the efficiency for the osmotic transport and swelling capacity, are added in the coupled formulation.

2 Balance laws for the open system

In a porous medium such as a rock or soil, an arbitrary sub-region V is studied, with boundary S assumed to be attached to the solid phases, ensuring no solid movement across the boundary,. Two fluxes, a water flux and a chemical flux, are allowed to pass the boundary. To simplify the analysis, (1) only one chemical in the water is considered and the chemical potential of the solute and water are μ^c and μ^w, respectively; (2) gas transport is ignored, but the unsaturated influence is still considered assuming that the gas phase is continuous in the unsaturated zone and remains at atmospheric pressure, $p_{atm} = 0$ [33, 34].

2.1 Flux and density

The flux (chemical/water) may be defined as

$$\mathbf{I}^\beta = \rho^\beta (\mathbf{v}^\beta - \mathbf{v}^s) \tag{1}$$

In which $\mathbf{I}^\beta$ is the flux of fluid β ($\beta=w$ denotes water, and $\beta=c$ denotes chemical), ρ^β and $\mathbf{v}^\beta$

are density and velocity, respectively. $\mathbf{v}^s$ represents the velocity of the solid phase.

The total fluid mass density ρ^f can be defined as

$$\rho^f = \rho^w + \rho^c \tag{2}$$

The fluid barycentric velocity may then be defined as the mass flux divided by the mass density, that is

$$\mathbf{v}^f = (\rho^w / \rho^f)\mathbf{v}^w + (\rho^c / \rho^f)\mathbf{v}^c \tag{3}$$

Since the diffusive fluxes of the water and chemical, relative to the barycentric motion, can be written as

$$\mathbf{J}^\beta = \rho^\beta (\mathbf{v}^\beta - \mathbf{v}^f) \tag{4}$$

the relationship between $\mathbf{I}^\beta$ and $\mathbf{J}^\beta$ is

$$\mathbf{J}^\beta = \mathbf{I}^\beta - \rho^\beta (\mathbf{v}^f - \mathbf{v}^s) \tag{5}$$

2.2 Balance equations for thermodynamically open system

The balance equations for the open system have been discussed in detail in [35], but to complete the analysis, the details are repeated here. The balance equation for Helmholtz free energy may be obtained as [11, 35]

$$\frac{D}{Dt}\left(\int_V \psi dV\right) = -\int_S \boldsymbol{\sigma}\mathbf{n} \cdot \mathbf{v}^s dS \ - \int_S (\mu^w \mathbf{I}^w + \mu^c \mathbf{I}^c) \cdot \mathbf{n}dS - T\int_V \gamma dV \tag{6}$$

where ψ is the Helmholtz free energy density, $\boldsymbol{\sigma}$ is the Cauchy stress tensor, $\mathbf{n}$ is the outward unit normal vector, T is the constant temperature and γ is the entropy production per unit volume, and where the material time derivative is given by

$$\frac{D}{Dt} = \partial_t + \mathbf{v}^s \cdot \nabla \tag{7}$$

Since there is no solid mass flux into the sub-region, the balance equation for the solid is

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$$\frac{D}{Dt}\left(\int_V \rho^s dV\right) = 0 \tag{8}$$

where the solid density is denoted by ρ^s.

Because V is open with respect to the exchange of fluid mass (water and chemical), the balance equation for the fluid can be expressed as

$$\frac{D}{Dt}\left(\int_V \rho^\beta dV\right) = -\int_S \mathbf{I}^\beta \cdot \mathbf{n} dS \tag{9}$$

2.3 Localized version of balance equations

The balance equation for the free energy can be obtained by using Reynold's transport theorem, as

$$\dot{\psi} + \psi \nabla \cdot \mathbf{v}^s - \nabla \cdot (\boldsymbol{\sigma} \mathbf{v}^s) + \nabla \cdot (\mu^w \mathbf{I}^w + \mu^c \mathbf{I}^c) = -T\gamma \leq 0 \tag{10}$$

The balance equation for the solid mass is

$$\dot{\rho}^s + \rho^s \nabla \cdot \mathbf{v}^s = 0 \tag{11}$$

and for fluid components is

$$\dot{\rho}^\beta + \rho^\beta \nabla \cdot \mathbf{v}^s + \nabla \cdot \mathbf{I}^\beta = 0 \tag{12}$$

The fluid component mass density ρ^β can be expressed relative to the unit volume of the fluid-solid mixture. Specifically, it is related to the true mass density ρ_t^β through

$$\rho^\beta = \phi^\beta \rho_t^\beta \tag{13}$$

where ϕ^β is the volume fraction of the relevant fluid component. If S^f is the saturation of the fluid, the relationship between ϕ^β and the porosity of the medium ϕ is given by

$$\sum \phi^\beta = S^f \phi \tag{14}$$

3 Entropy production and extension of Darcy's Law

3.1 Entropy production

Based on the assumption that only one dissipation mechanism is generated due to the friction at the solid/fluid boundary, by using standard arguments of non-equilibrium thermodynamics [36], the dissipation generated may be described as

$$0 \leq T\gamma = -\mathbf{I}^{\mathrm{w}} \cdot \nabla \mu^{\mathrm{w}} - \mathbf{I}^{\mathrm{c}} \cdot \nabla \mu^{\mathrm{c}} \tag{15}$$

As Darcy velocity can be expressed as

$$\mathbf{u} = S^{\mathrm{f}}\phi(\mathbf{v}^{\mathrm{f}} - \mathbf{v}^{\mathrm{s}}) \tag{16}$$

then, by introducing equation (5), the entropy production of the fluid can be written as

$$0 \leq T\gamma = -\mathbf{u} \cdot \nabla \mathrm{p} - (\mathbf{J}^{\mathrm{w}} \cdot \nabla \mu^{\mathrm{w}} + \mathbf{J}^{\mathrm{c}} \cdot \nabla \mu^{\mathrm{c}}) \tag{17}$$

There is a direct relationship between $\mathbf{J}^{\mathrm{c}}$ and $\mathbf{J}^{\mathrm{w}}$, as they have to satisfy

$$\mathbf{J}^{\mathrm{w}} + \mathbf{J}^{\mathrm{c}} = 0 \tag{18}$$

The Gibbs-Duhem equation for the fluid can also give the relationship between $\mathrm{p}_{\mathrm{pore}}$ and $\nabla \mu^{\mathrm{c}}$ as

$$\rho_{\mathrm{t}}^{\mathrm{w}} \nabla \mu^{\mathrm{w}} + \rho_{\mathrm{t}}^{\mathrm{c}} \nabla \mu^{\mathrm{c}} = \nabla \mathrm{p}_{\mathrm{pore}} \tag{19}$$

where $\mathrm{p}_{\mathrm{pore}}$ denotes the pore pressure of the fluid mixture (that is, of the water, chemical and gas combined). Note that the gas chemical potential is assumed to be zero in equation (18) [37]. Based on above analysis, the entropy production leads to

$$0 \leq T\gamma = -\mathbf{u} \cdot \nabla \mathrm{p} - \mathbf{J}^{\mathrm{c}} \cdot \nabla(\mu^{\mathrm{c}} - \mu^{\mathrm{w}}) \tag{20}$$

3.2 Phenomenological equations

Phenomenological equations can be used to obtain the linear relationship between flows and corresponding driving forces [36]. The relationship of Darcy flow and the major driving force

∇p, the diffusive flow $\mathbf{J}^c$ and the major driving force $\nabla(\mu^c - \mu^w)$ may be described as

$$\rho_t^f \mathbf{u} = -(L^{11} / \rho_t^f)\nabla p - L^{12}\nabla(\mu^c - \mu^w) \tag{21}$$

$$\mathbf{J}^c = -(L^{21} / \rho_t^f)\nabla p - L^{22}\nabla(\mu^c - \mu^w) \tag{22}$$

where L^{ij} denotes a set of phenomenological coefficients. In the above equations, the coupling influence of driving force on the flow can be included. Here, the mass transport is assumed to be through an isotropic medium.

3.3 Chemical potential and chemical concentration

The relationship of chemical potential and chemical concentration can be obtained by using the Gibbs-Duhem equation [36] for the fluid at constant pressure as

$$C^c(d\mu^c)_p + C^w(d\mu^w)_p = 0 \tag{23}$$

where C^c and C^w are the solute and diluent mass fractions, respectively, which can be defined as

$$C^c = \rho_t^c / \rho_t^f = \rho^c / \rho^f, \ C^w = \rho_t^w / \rho_t^f = \rho^w / \rho^f \tag{24}$$

Also,

$$\nabla(\mu^c - \mu^w) = (\upsilon^c - \upsilon^w)\nabla p + \frac{1}{C^w}\frac{\partial \mu^c}{\partial C^c}\nabla C^c \tag{25}$$

where $\upsilon^c = \dfrac{\partial(1/\rho_t^c)}{\partial C^c}$ and $\upsilon^w = \dfrac{\partial(1/\rho_t^w)}{\partial C^w}$ denote the partial specific volumes of the solute and diluent, respectively. These quantities satisfy the thermodynamic identities,

$$\upsilon^c = \frac{\partial(\mu^c)}{\partial p}, \ \upsilon^w = \frac{\partial(\mu^w)}{\partial p} \tag{26}$$

In addition, if $\rho_t^f(\upsilon_f^c - \upsilon_f^w) \square \ 1$, then equations (21) and (22) can be rewritten as

$$\mathbf{u} = -k\frac{k_{rw}}{\theta}(\nabla p - r\frac{\rho_t^f}{C^w}\frac{\partial \mu^c}{\partial C^c}\nabla C^c) \tag{27}$$

$$\mathbf{J}^c = L\rho_t^f \frac{\nabla p}{p} - \rho_t^f D \nabla C^c \tag{28}$$

where

$$k\frac{k_{rw}}{\theta} = \frac{L^{11}}{\left(\rho_t^f\right)^2}, \quad r = -\frac{L^{21}}{L^{11}}, \quad L = \frac{L^{21} p}{\left(\rho_t^f\right)^2}, \quad D = \frac{L^{22}}{C^w \left(\rho_t^f\right)^2} \frac{\partial \mu^c}{\partial C^c} \tag{29}$$

and θ is the fluid's dynamic viscosity.

4 Equations of state

4.1 Basic equation of state

Based on the assumption that the rock maintains mechanical equilibrium, and also in the absence of volume forces, $\nabla \cdot \boldsymbol{\sigma} = \mathbf{0}$, by using equations (10), ψ can be written as

$$\dot{\psi} + \psi \nabla \cdot \mathbf{v}^s - \left(\boldsymbol{\sigma} : \nabla \mathbf{v}^s \right) + \mu^w \nabla \cdot \mathbf{I}^w + \mu^c \nabla \cdot \mathbf{I}^c = 0 \tag{30}$$

By using continuum mechanics and equations (30), this leads to

$$\dot{\Psi} = \mathrm{tr}\,(\mathbf{T}\dot{\mathbf{E}}) + \mu^w \dot{\mathrm{m}}^w + \mu^c \dot{\mathrm{m}}^c \tag{31}$$

$$\Psi = \mathrm{J}\psi, \; \mathrm{m}^\beta = \mathrm{J}\rho^\beta = \mathrm{J}\phi^\beta \rho_t^\beta \tag{32}$$

where Ψ is the free energy in the reference configuration, and m^β is the mass density of the fluid component in the reference configuration. The deformation state of the porous media, based on continuum mechanics, may be described as follows:

If $\mathbf{X}$ is an arbitrary reference configuration with a position $\mathbf{x}$ at time t, the relationships between the Green strain $\mathbf{E}$, deformation gradient $\mathbf{F}$, second Piola-Kirchhoff stress $\mathbf{T}$ and J (the Jacobian of $\mathbf{F}$) are

$$\mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}}(\mathbf{X},\mathrm{t}), \; \mathbf{E} = \frac{1}{2}(\mathbf{F}^{\mathrm{T}}\mathbf{F} - \mathbf{I}), \; \mathrm{J} = \frac{\mathrm{dV}}{\mathrm{dV}_0}, \; \dot{\mathrm{J}} = \mathrm{J}\nabla \cdot \mathbf{v}^s, \; \mathbf{T} = \mathrm{JF}^{-1}\boldsymbol{\sigma}\mathbf{F}^{-\mathrm{T}} \tag{33}$$

4.2 Helmholtz free energy density of fluids

The pore fluids exist in both pore space and clay platelets. Thermodynamic relationships can only be used for the bulk fluids in the pore spaces, hence the Helmholtz free energy density of the pore fluid, ψ_{pore}, can be rearranged as

$$\psi_{\mathrm{pore}} = -\mathrm{p}_{\mathrm{pore}} + \mu^c \rho_t^c + \mu^w \rho_t^w \tag{34}$$

where $\mathrm{p}_{\mathrm{pore}}$ is the pore pressure.

According to the Gibbs-Duhem equation, this leads to

$$\dot{p}_{pore} = \dot{\mu}^c \rho_t^c + \dot{\mu}^w \rho_t^w \tag{35}$$

From equation (34)

$$\dot{\psi}_{pore} = -\dot{p}_{pore} + \dot{\mu}^c \rho_t^c + \dot{\mu}^w \rho_t^w + \mu^c \dot{\rho}_t^c + \mu^w \dot{\rho}_t^w \tag{36}$$

Hence, by introducing equation (35) this leads to

$$\dot{\psi}_{pore} = \mu^c \dot{\rho}_t^c + \mu^w \dot{\rho}_t^w \tag{37}$$

4.3 Free energy density of the solid matrix

The total free energy Ψ Can be viewed as the combination of (1) the free energy of the combined solid/fluid matrix including water bounded between clay platelets, which may be named as "wet matrix", and (2) the contribution of the pore fluid. Then the free energy of the "wetted matrix" can be obtained. Note the influence of gas has been ignored here to simplify the discussion, but the unsaturated influence has been included in the p_{pore}.

$$(\Psi - J\phi\psi_{pore}\dot{)} = tr(\mathbf{T\dot{E}}) + p_{pore}\dot{\upsilon} + \mu^w \dot{m}_{bound}^w \tag{38}$$

where $\upsilon = J\phi$ is pore volume per unit referential volume, $m_{bound}^w = m^w - JS_w\phi\bar{\rho}_{pore}^w$ is the referential mass density of the bound water. Then dual potential can be written as

$$W = (\Psi - J\phi\psi_{pore}) - p_{pore}\upsilon - \mu^w m_{bound}^w \tag{39}$$

By expressing W as a function of $\mathbf{E}$ and p_{pore} and μ^w, the expressions for $\mathbf{T}$, υ and m_{bound}^w can be derived. Equation (39) implies that the time derivative of $W(E, p_{pore})$ satisfies the relationship

$$\dot{W}(\mathbf{E}, p, \mu) = tr(\mathbf{T\dot{E}}) - \dot{p}_{pore}\upsilon - \dot{\mu}^w m_{bound}^w \tag{40}$$

so that

$$T_{ij} = \left(\frac{\partial W}{\partial E_{ij}} \right)_{P_{pore},\mu^w} \quad , \quad \upsilon = -\left(\frac{\partial W}{\partial p_{pore}} \right)_{E_{ij},\mu^w} \quad , \quad m^w_{bound} = -\left(\frac{\partial W}{\partial \mu^w} \right)_{E_{ij},\bar{p}} \tag{41}$$

and also

$$\dot{W}(\mathbf{E}, p) = \left(\frac{\partial W}{\partial E_{ij}} \right)_{P_{pore},\mu^w} \dot{E}_{ij} + \left(\frac{\partial W}{\partial p_{pore}} \right)_{E_{ij},\mu^w} \dot{p}_{pore} + \left(\frac{\partial W}{\partial \mu^w} \right)_{E_{ij},p} \dot{\mu}^w \tag{42}$$

The fundamental constitutive equations for the evolution of stress, pore volume fraction and mass of bounded water can be obtained by differentiating equations (41) with respect to time to give

$$\dot{T}_{ij} = L_{ijkl}\dot{E}_{kl} - M_{ij}\dot{p}_{pore} - S_{ij}\dot{\mu}^w \tag{43}$$

$$\dot{\upsilon} = M_{ij}\dot{E}_{ij} + Q\dot{p}_{pore} + B\,\dot{\mu}^w \tag{44}$$

$$\dot{m}^w_{bound} = S^k_{ij}\dot{E}_{ij} + B^k\dot{p}_{pore} + Z\,\dot{\mu}^w \tag{45}$$

where the parameters L_{ijkl}, M_{ij}, S_{ij}, Q, B, Z are defined by the following equations:

$$L_{ijkl} = \left(\frac{\partial T_{ij}}{\partial E_{kl}} \right)_{P_{pore},\mu^w} = \left(\frac{\partial T_{kl}}{\partial E_{ij}} \right)_{P_{pore},\mu^w}$$

$$M_{ij} = -\left(\frac{\partial T_{ij}}{\partial p_{pore}} \right)_{E_{ij}} = \left(\frac{\partial \upsilon}{\partial E_{ij}} \right)_{P_{pore}}$$

$$S^k_{ij} = \left(\frac{\partial T_{ij}}{\partial \mu^k} \right)_{E_{ij},p} = -\left(\frac{\partial m^l_{bound}}{\partial E_{ij}} \right)_{p,\mu^w}$$

$$Z^{kl} = \left(\frac{\partial m^k_{bound}}{\partial \mu^l} \right)_{E_{ij},p,\mu^w} = \left(\frac{\partial m^l_{bound}}{\partial \mu^k} \right)_{E_{ij},p,\mu^w}$$

$$B^k = \left(\frac{\partial \upsilon}{\partial \mu^k} \right)_{E_{ij},p} = \left(\frac{\partial m^k_{bound}}{\partial p_{pore}} \right)_{E_{ij},\mu^w}$$

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$$Q = \left(\frac{\partial \upsilon}{\partial \mathrm{p}_{\mathrm{pore}}} \right)_{\mathrm{E}_{\mathrm{ij}} , \mu^{\mathrm{w}}} \tag{46}$$

5 Chemical potential and transport

The chemical potentials relationship may be obtained from equation (35)

$$\dot{\mu}^w = (\frac{1}{\rho_t^w})\left(\dot{p}_{pore} - \rho_t^c \dot{\mu}^c\right) \qquad (47)$$

The thermodynamic expression of solute chemical potential is given by the expression [36]

$$\mu^c = g^c(p,T) + (\frac{RT}{M^c})(\ln a^c) \qquad (48)$$

where R is the gas constant, M^c is the molar mass of the chemical, a^c is the activity of the solute which is a measure of the 'effective concentration' of the solute in the mixture, and g^c is a function that depends on pressure and temperature, which can be normally neglected because the dependence of μ^c on g^c is very weak. The relationship between a^c and x^c can be described as

$$a^c = r_c x^c \qquad (49)$$

where r_c is the activity coefficient, which can be described as $r_c = 1$ if the solution is assumed to be ideal, so that the solute activity $a^c = x^c$. Note that the mole fraction x^c is related to the solute mass fraction C^c through

$$C^c = x^c M^c /(x^c M^c + (1-x^c)M^w) \qquad (50)$$

The chemical transport equation may be derived by using the partial mass equation (12), the mass density equation (13), equation (5) and the Euler identity:

$$(S^f \upsilon \rho_t^{\beta \cdot}) + J\nabla \cdot (\rho^\beta \mathbf{u}) + J\nabla \cdot \mathbf{J}^\beta = 0 \qquad (51)$$

By introducing the mass fraction $C^\beta = \rho_t^\beta / \rho_t^f$ and assuming the fluid to be incompressible, equation (51) can be rewritten as

$$(S^f \upsilon \rho_t^f C^{\beta \cdot}) + \nabla \cdot (\rho_t^f C^\beta \mathbf{u}) + \nabla \cdot \mathbf{J}^\beta = 0 \qquad (52)$$

Further consideration with $\sum_\beta C^\beta = 1$ and $\sum_\beta \mathbf{J}^\beta = 0$, and summing over all the fluid

components leads to the relationship

$$(\upsilon S^f \rho_t^f \dot) + \nabla \cdot (\rho_t^f \mathbf{u}) = 0 \tag{53}$$

By invoking equation (53), equation (52) can be transformed to

$$(\upsilon S^f \rho_t^f) \dot{C}^\beta + \rho_t^f \mathbf{u} \cdot \nabla C^\beta + \nabla \cdot \mathbf{J}^\beta = 0 \tag{54}$$

6 Final constitutive equations

Equations (43) and (44), (45) show the general constitutive equations for multiphase flow in porous rock/soils. To simply the discussion, further assumptions are made based on physical and geometrical linearisation: (1) material non-linearity is not considered here the and non-linearity is only of a geometrical nature and associated with large deformations, leading to the assumption that the parameters L_{ijkl}, M_{ij} and Q are material-dependent constants. (2) small strain is adopted here so that Green Strain tensor E_{ij} and the Piola-Kirchhoff stress T_{ij} can be replaced by the strain tensor ε_{ij} and Cauchy stress σ_{ij}, that is

$$E_{ij} = \varepsilon_{ij}, \; T_{ij} = \sigma_{ij} \tag{55}$$

(3) material isotropy is assumed here so that the tensor M_{ij} is diagonal and can be written in terms of scalar ζ

$$M_{ij} = \zeta \delta_{ij} \tag{56}$$

and the elastic stiffness L_{ijkl} can be formed as a fourth-order isotropic tensor,

$$L_{ijkl} = G(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + (K - \frac{2G}{3})\delta_{ij}\delta_{kl} \tag{57}$$

in which G is the rock shear modulus and *K* is the bulk modulus.

6.1 Solid phase

The defined changes in solid stress, volume fraction and bound water mass are described in equations (43) and (44) and (45) with independent variables, such as $\varepsilon_{ij} = \frac{1}{2}(d_{i,j} + d_{j,i})$ in which $d_{i,j}$ (*i,j*=1,2,3) is the displacement component, the pore fluid pressure p and the solute mole fraction x^s.

If mechanical equilibrium is assumed, then

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0 \tag{58}$$

This leads to rearrangement of the solid phase and pore volume fraction equations as

$$\dot{\sigma}_{ij} = (K - \frac{2G}{3})\dot{\varepsilon}_{kk}\delta_{ij} + 2G\dot{\varepsilon}_{ij} - \zeta \dot{p}\delta_{ij} + \omega^w \dot{\mu}^w \tag{59}$$

$$\dot{\upsilon} = \zeta \dot{\varepsilon}_{ii} + Q\dot{\bar{p}} + B^w \dot{\mu}^w \tag{60}$$

where the quantity ζ can be written related to the bulk moduli K and K_s in a poro-elastic manner as $\zeta = 1 - (K / K_s)$, and K_s is the bulk modulus of the solid matrix. The void compressibility Q is related to the scalar ζ according to

$$Q = (1/K_s)(\zeta - \phi) \tag{61}$$

From equation (43), this leads to

$$G\nabla^2 \dot{\mathbf{d}} + \left(\frac{G}{1-2\nu}\right)\nabla(\nabla \cdot \dot{\mathbf{d}}) + \omega^D \frac{\partial}{\partial x_i}\left(\frac{1}{\bar{\rho}^D}\right)\frac{\partial \bar{p}}{\partial t} - \left(\zeta - \frac{\omega^D}{\bar{\rho}^D}\right)\frac{\partial}{\partial x_i}\left(\frac{\partial \bar{p}}{\partial t}\right) = 0 \tag{62}$$

The average pore pressure $\bar{p}$ in equation (62) is assumed to equal the pore pressure p_{pore} in the mechanical equilibrium condition and, by assuming gas pressure can be ignored, this leads to

$$\bar{p} = S^f p \tag{63}$$

where p is the pore fluid pressure.

Lewis and Scherefler (1987) [18] discussed the time derivative of $\bar{p}$ as

$$\dot{\bar{p}} = S^f \frac{\partial p}{\partial t} + \frac{C_s}{\phi} p \frac{\partial p}{\partial t} \tag{64}$$

where C_s is the specific moisture content, which is defined in terms of pressure. Hence, by using the definition of average pressure in equation (64),

(65)

$$G\nabla^2 \mathbf{d} + \left(\frac{G}{1-2\nu}\right)\nabla(\nabla \cdot \mathbf{d}) + \omega^D \nabla\left[\frac{1}{\bar{\rho}^D}(S^f + \frac{C_s}{\phi}p)\dot{p}\right] - \left(\zeta - \frac{\omega^D}{\bar{\rho}^D}\right)\nabla\left[(S^f + \frac{C_s}{\phi}p)\dot{p}\right] = 0$$

6.2 Fluid phase

The equation for water transport with consideration of chemical osmosis may be obtained from equations (53) and (60) as

$$S^f \rho_t^f \zeta \nabla \cdot \dot{\mathbf{d}} + S^f \rho_t^f Q\dot{p} + \phi\rho_t^f \frac{\partial S^f}{\partial t} + \phi S^f \frac{\partial \rho_t^f}{\partial t} + \rho_t^f\left[-\nabla \cdot k\frac{k_{rw}}{\theta}(\nabla p - \rho_t^f r\frac{RT}{M^c}\frac{1}{C^c C^w}\nabla C^c)\right] = 0$$

(66)

By considering the rate of change of saturation and the water density function [18],

$$\phi\frac{\partial S^f}{\partial t} + \frac{\phi S^f}{\rho_t^f}\frac{\partial \rho_t^f}{\partial t} = C_S\frac{\partial p}{\partial t} + \phi\frac{S^f}{K_w}\frac{\partial p}{\partial t} = (C_S + \phi\frac{S^f}{K_w})\frac{\partial p}{\partial t} \qquad (67)$$

where K_w is the bulk modulus of water, equation (66) can be rewritten as

$$S^f \zeta \nabla \cdot \dot{\mathbf{d}} + S^f Q(S^f + \frac{C_s}{\phi}p)\frac{\partial p}{\partial t} + (C_S + \phi\frac{S^f}{K_w})\frac{\partial p}{\partial t} + \left[-\nabla \cdot k\frac{k_{rw}}{\theta}(\nabla p - \rho_t^f r\frac{RT}{M^c}\frac{1}{C^c C^w}\nabla C^c)\right] = 0$$

(68)

6.3 Chemical transport

From equations (27), (28) and (54), the chemical transport equation can be obtained as

$$S^f \phi\dot{C}^c - \left[k\frac{k_{rw}}{\theta}(\nabla p - \rho_t^f r\frac{RT}{M^c}\frac{1}{C^c C^w}\nabla C^c)\right]\cdot\nabla C^c - L\nabla\left(\frac{1}{p}\nabla p\right) - D\nabla^2 C^c = 0 \quad (69)$$

7 Numerical simulation

A simple one-dimensional model, which is similar to Heidug and Wong [6] and Chen and Hicks [31] was developed to demonstrate hydration swelling coupled with unsaturated chemical osmotic flow. The material parameter values in Table 1 were selected from the Tournemire site [38], with additional assumptions of osmotic reflection parameters and hydration swelling parameters.

The geometry and boundary conditions of the numerical experiment are described in Fig 1. An increment of chemical mass fraction was applied to boundary A with initially unsaturated and free chemical in a plane rock specimen. The rock sample was assumed to be a non-swelling rock firstly, and then replaced with a swelling sample for comparison. Chemical transport will occur from boundary A, through which water will also flow out. During this process, coupled water and chemical transport will impose a different impact on the rock deformation, with different response for the non-swelling and swelling rock sample. The numerical simulation demonstrates the difference in due course.

In the finite element analysis used for the numerical simulation, 60 equal-sized rectangular composite elements were used, with eight nodes for the displacement field and four nodes for pore fluid pressure and chemical mass fraction [31]. The initial and boundary conditions are set as the same in the example proposed by [31]: initially, the system is in mechanical equilibrium and the effective stress is zero, the pore fluid pressure is -4MPa with a corresponding saturation of 0.9951, following the van Genuchten [39] relationship. Boundary A is freely permeable, and the chemical mass fraction is increased from 0 to 0.35 at the beginning.

Time points of 40 hours and 400 hours, which represent short and long term periods, were selected to analyse the results. The chemical mass fraction increases with time in both the non-swelling and swelling rock [Fig 2]. For this paper attention was focused on the effect of hydration swelling on the mechanical performance; the influence of swelling on the porosity change was ignored to simply the discussion. Thus, the chemical transport for both swelling and non-swelling rock scenarios is identical [Fig 2].

The influence of swelling on the mechanical performance during chemical osmosis is shown in Fig [3]. The displacement keeps increasing over time from 40 to 400 hours. However, the swelling rock has a better resistance to consolidation, demonstrated by less displacement in the same time point. The effective stress difference in Fig [4] shows an insight overlook of the difference for displacement change. The effective stress for swelling rock is less than that for the non-swelling rock. This is because swelling potential caused by the molecular water in clay platelets resists to consolidation (section 4.2 in this paper).

The degree of saturation remains the same for swelling and non-swelling rock, as the molecular water absorbed into the clay platelets may be a very small amount in a nearly saturated condition, compared with the water volume in the pore space. In this analysis, the swelling coefficient is assumed to be 0.2, although in some highly swelling material the absorbed water may need to be taken into account for future research. As this study focused on the influence of swelling, the analysis related to chemical osmosis, which can found in Chen & Hicks [31], will not be duplicated here.

8 Conclusions

In this study, Mixture Coupling theory has been further extended by including hydration swelling into chemical osmosis, resulting in a new constitutive unsaturated coupled hydro-mechanical-chemical model. Modified Mixture theory has the potential to bridge geophysics and geochemistry under a single unified theory. By using non-equilibrium thermodynamics, the mechanical energy and fluid energy have been combined for the analysis.

Hydration swelling and chemical osmosis in an unsaturated condition may have an important engineering application, such as nuclear waste disposal, in which the clay material used as a barrier to encapsulate the waste may swell, and function as a semi-permeable membrane. Another example is shale borehole drilling, in which both the swelling and osmosis may be important for instability problem of borehole wall. The new mathematical model presented in this paper may provide a more accurate modelling tool for such engineering problems. The simple numerical simulation in this paper clearly demonstrates the important influence of hydration swelling in unsaturated low permeability rock. However a more sophisticated engineering application model may be needed in due course. Further research is needed to study the porosity change in highly swelling materials, as pore water pressure may affect the porosity.

Acknowledgements

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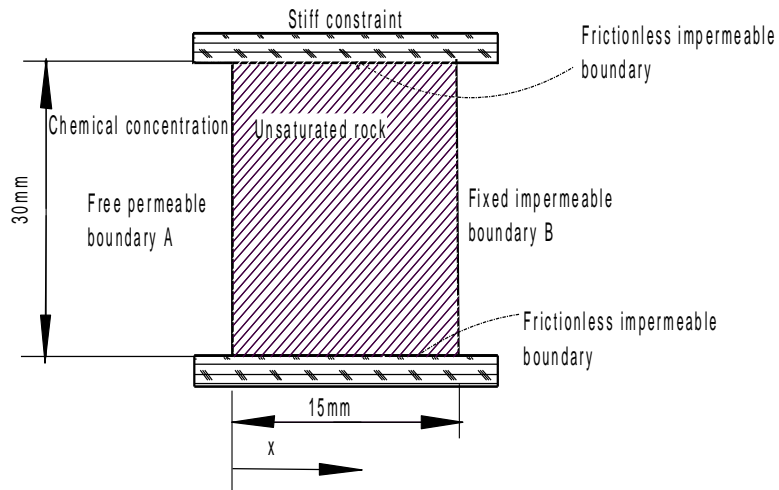
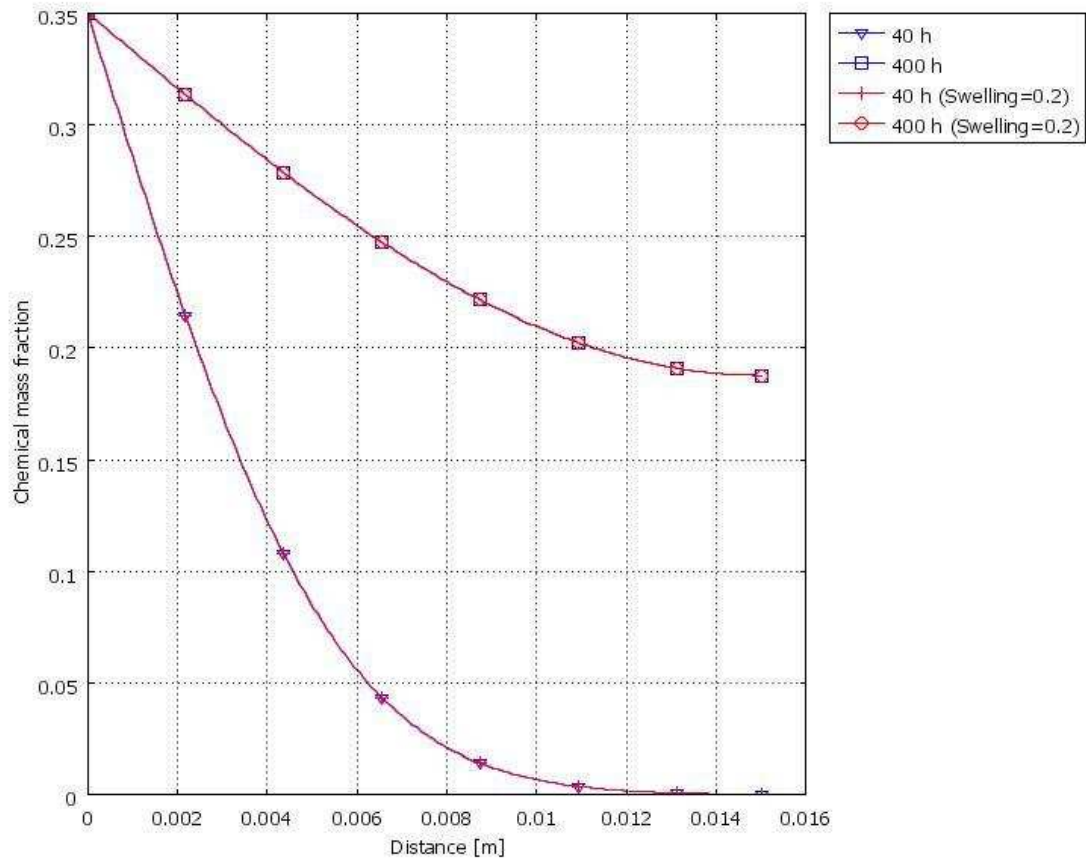Fig 1 Unsaturated rock analysis (not to scale)

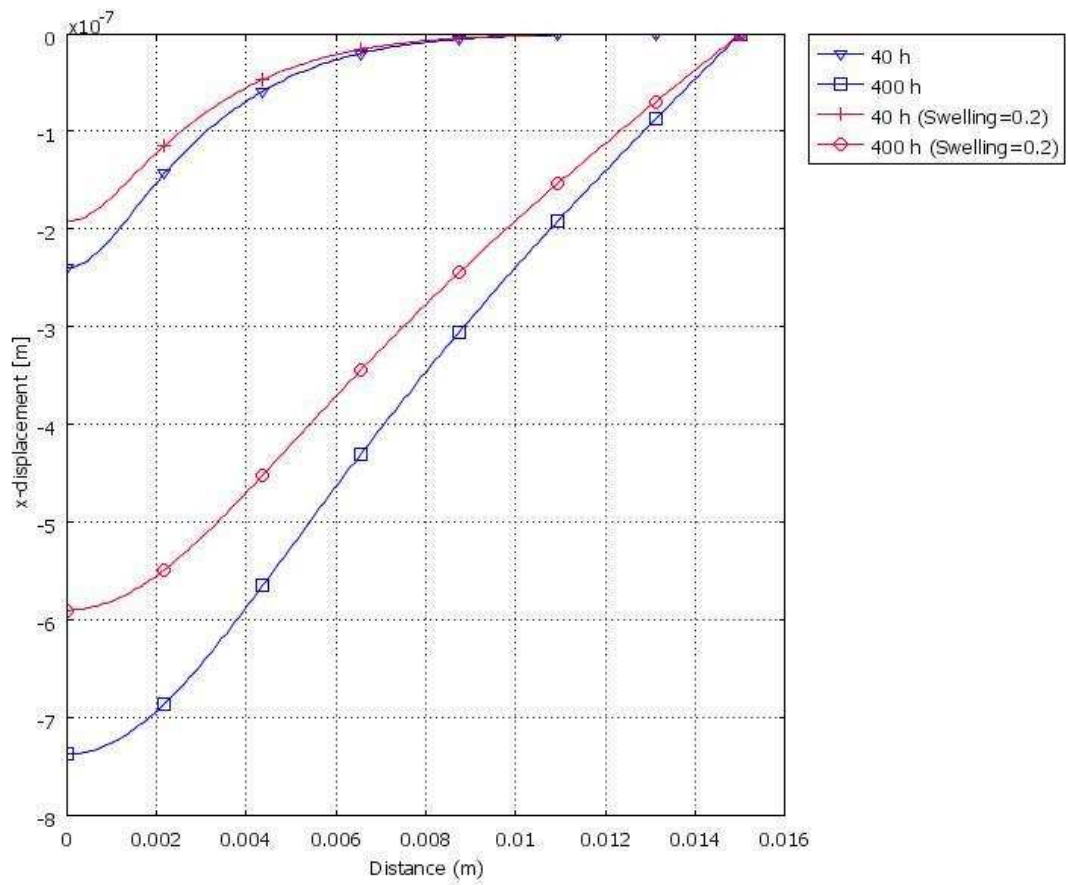Fig 2 Evolution of chemical mass fraction distribution with time

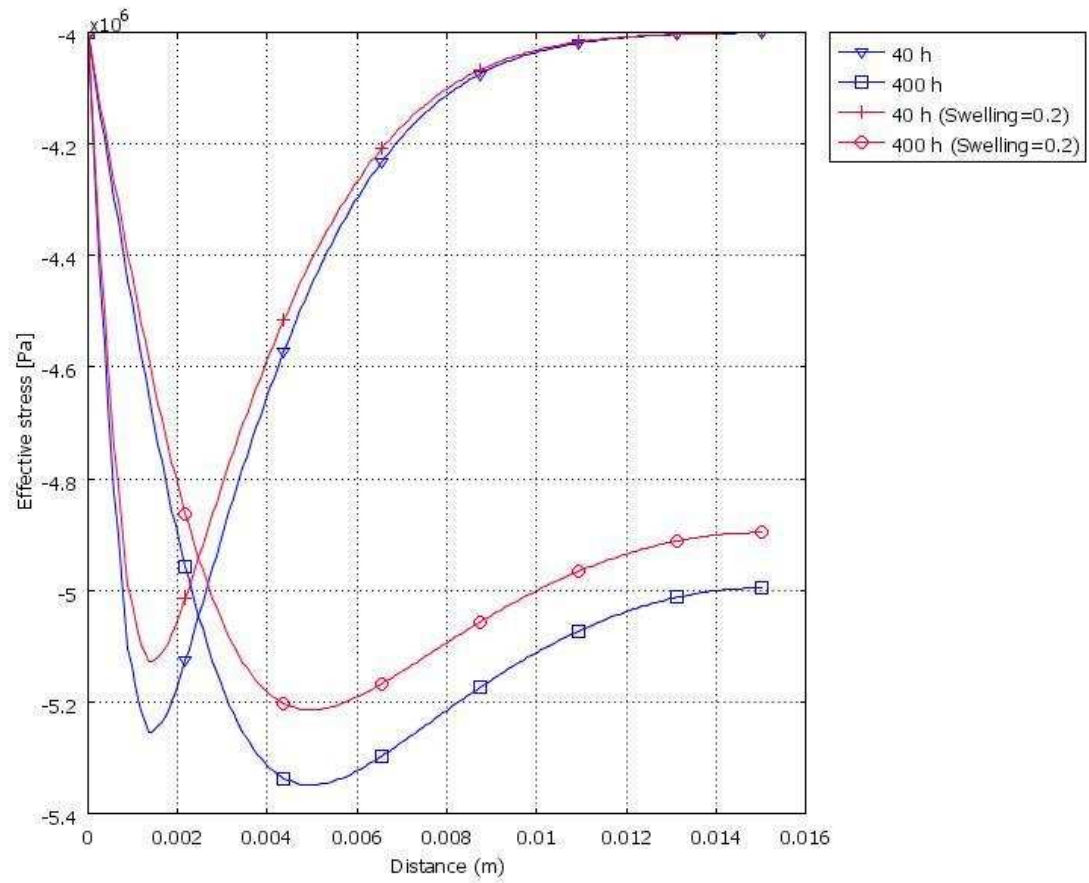Fig 3 Evolution of horizontal displacement distribution with time

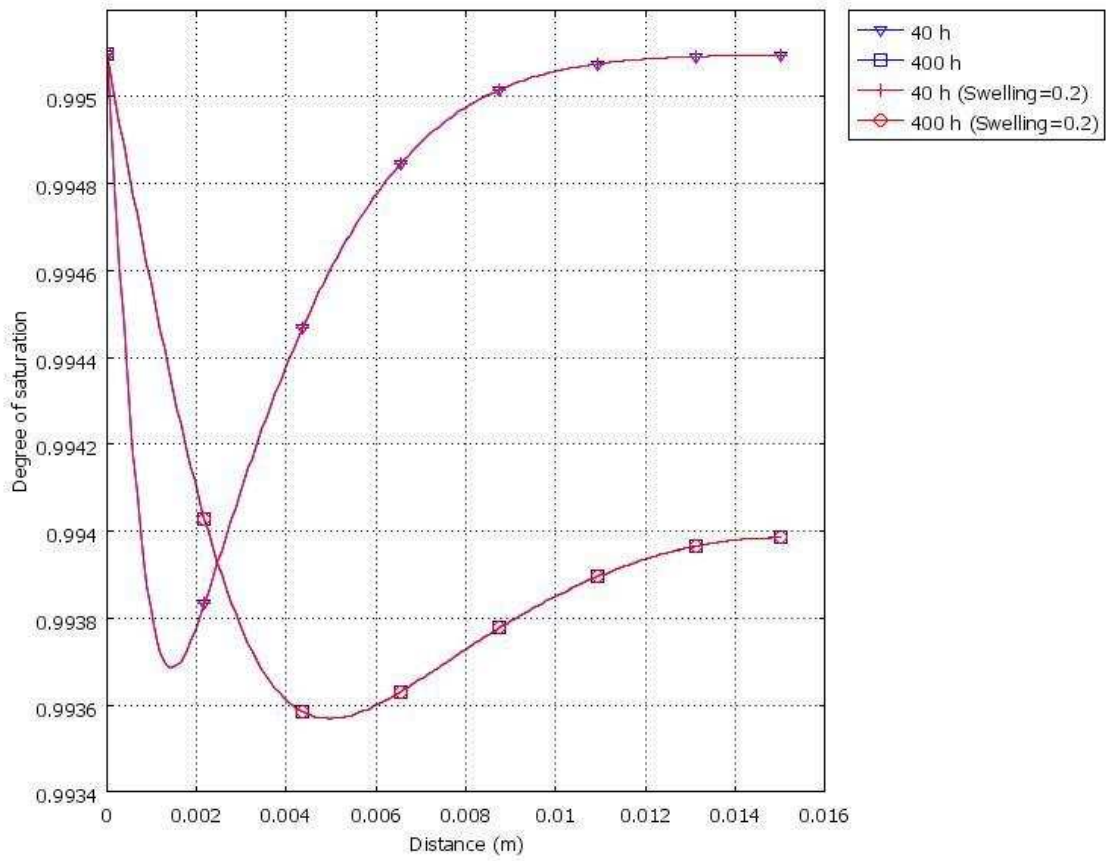Fig 4 Evolution of horizontal effective stress distribution with time

Fig 5 Evolution of degree of saturation distribution with time

Table 1 Material parameters of host rock for nuclear waste disposal [27]

Parameters	Physical meaning	Values and units
Hydraulics		
ρ_t^w	Density of water	1000 kg/m^3
k/θ	Absolute Permeability/Dynamic viscosity	10^{-13} m/s [2]
m	Van Genuchten parameter	0.43
M	Van Genuchten parameter	51 MPa
Mechanics		
E	Young's modulus	9720 MPa
v	Poisson's ratio	0.2
Chemical		
D	Diffusion coefficient	$3.2*10^{-12}$ m^2/s [2]
r	Reflection coefficient	0.1 [6]
Coupling		
ζ	Biot coefficient	1.0
Q	Void compressibility	0.000005 MPa^{-1}