Article:

Ma, Y, Chen, X, Hosking, LJ et al. (2022) THMC constitutive model for membrane geomaterials based on Mixture Coupling Theory. International Journal of Engineering Science, 171. 103605. ISSN: 0020-7225

https://doi.org/10.1016/j.ijengsci.2021.103605

THMC constitutive model for membrane geomaterials based on Mixture Coupling Theory

Yue Ma[1], Xiaohui Chen[1]*, Lee J. Hosking[2], Hai-Sui Yu[1], Hywel R. Thomas[3]

[1]School of Civil Engineering, University of Leeds, LS2 9JT, UK

[2]Department of Civil and Environmental Engineering, Brunel University London, Uxbridge, Middlesex UB8 3PH, UK

[3]Geoenvironmental Research Centre, School of Engineering, Cardiff University, Cardiff CF24 3AA, UK

*x.chen@leeds.ac.uk

---

[1] * Correspondence to: X. Chen, School of Civil Engineering, University of Leeds, LS2 9JT, UK
E-mail: x.chen@leeds.ac.uk

THMC constitutive model for membrane geomaterials based on Mixture Coupling Theory

Abstract

Modelling of coupled thermal (T), hydro (H), mechanical (M) and chemical (C) processes in geomaterials has attracted attention in the past decades due to many significant contemporary engineering applications such as nuclear waste disposal, carbon capture and storage etc. However, in very-low permeability membrane geomaterials, the couplings between chemical osmosis and thermal osmosis and their consequent influence on temperature, water transport and mechanical deformation remain as a long-lasting challenge due to the gap between geomechanics and geochemistry. This paper extends Mixture Coupling Theory by bridging the chemical-thermal field based on non-equilibrium thermodynamics, and develops a new constitutive THMC fully-coupled model incorporating the interactions between chemical and thermal osmosis. Classic Darcy's law has been fundamentally extended with osmosis as the major driving force of the diffusion process. A simple numerical simulation used for the demonstration purpose has illustrated that the couplings between chemical and thermal osmosis will significantly change the water flow directions, consequently influencing the saturation variation and mechanical deformation.

Keywords: THMC model; Diffusion; Non-equilibrium thermodynamics; Thermo osmosis, Chemical osmosis;

1 Introduction

Very low permeability geomaterials can act as actual semi-permeable membranes, having good functions for chemical retardation or sorption [1]. They are widely used in engineering applications such as nuclear waste disposal, carbon capture and storage, landfill etc [2]. Due to the low permeability, hydraulic flow is not the dominant form of fluid movement [3]. Thermal and chemical gradients will induce fluid flux into or out of the formation, leading to thermal and chemical osmosis [4]. The chemical osmosis flow direction is from lower chemical concentration to higher chemical concentration, and maybe opposite to the pressure gradient-induced flow direction, thereby reducing the flow velocity [5]. Similarly, temperature gradient would also cause a thermal osmosis flow, which has been observed in different experiments [6, 7]. This kind of flow may occur from high temperature to low temperature or in the opposite direction [8], depending on the entropy difference between water in the membrane and external to the membrane[9].

Coupled thermal (T), hydraulic (H), mechanical (M) and chemical processes (C) have been studied mainly by three theoretical approaches, namely: the mechanics approach, the mixture theory approach, and Mixture Coupling Theory [10-12]. The mechanics approach is based on the classic consolidation theory of Terzaghi [13] and Biot [14, 15]. This approach focuses on the macroscopic process of THMC (e.g. pressure/displacement/concentration/temperature). This makes it very practical since the equations may be specially developed for the intended specific application without deep understanding of the microscopic mechanisms. A lot of research has been done using this approach [16-19]. However, the theoretical foundation of the mechanics approach has led to the difficulties of coupling of chemical processes (micro-process dominated), due to the gap between geophysics and geochemistry. The mechanics approach has tried to borrow uncoupled equations from other disciplines to form new governing equations to overcome the challenge. However, such governing equations are highly semi-empirical and rely heavily on experiments, hence they are not rigorously mathematically derived. Mixture theory was firstly developed by Truesdell [20] and further extended by Bowen [21, 22] and Rajagopal & Tao [23-25]. This approach gives detailed couplings between solids and fluids. Mixture theory maintains the individuality of the constituents, which has led to the difficulties of obtaining detailed interaction information between constituents and therefore restricted its application.

Mixture coupling theory originates from mixture theory, but adopts Biot's poroelasticity viewing a fluid-infiltrated rock/soil as a single continuum and employs thermodynamic force-flux couplings, rather than introducing body forces between the constituents in the constituent equilibrium equations (or constituent equations of motion in the general case) as in classic mixture theory [26]. This approach combines Biot's theory and non-equilibrium thermodynamics. It simplifies the variables of interactions between solids particles which are normally difficult to obtain in geomaterials, and enables incorporating the well-developed continuum mechanics for solids deformation. By using fundamental principles of non-equilibrium thermodynamics (e.g. entropy), mixture coupling theory is capable of mathematically building the coupling between energy and dynamics in the mixture system, and has the potential to smoothly bridge geomechanics and geochemistry [1, 2, 27-29].

In this paper, a new coupled THMC formulation has been developed by extending mixture coupling theory. Classic Darcy's law has been extended to include coupled chemical osmosis and thermal osmosis through using standard arguments of non-equilibrium thermodynamics. Helmholtz free energy has been used to derive the relationship between solid and fluid phase and thermal behaviour. A simple numerical model has been given to illustrate the influence of chemical osmosis and thermal osmosis.

2 Balance and Conservation Equations

The mixture within a porous medium contains β states of matter which may include solids (denoted as subscript *s*), liquids (*l*), and gases (*g*); α constituents ($\alpha = 1:n$) which may include examples as water (denoted as *w*) or chemicals (as *c* in general). One state of matter may consist of multiple constituents, if there is only one constituent in a matter state, it leads to a simplified $\beta = \alpha$. *V* is a selected microscopic volume of an arbitrary domain within the porous medium and *S* is its boundary that is attached to the solid matter. *V* is assumed to be big enough to include all types of constituents present in the local region, and there is no movement of solids across the domain boundary *S*; only movement of fluids (including chemicals in the liquid) or energy (e.g. thermal). The gases' contribution to the pore pressure (as well as the mass) is ignored to simplify the discussion [30, 31], as this research is focused on osmosis in a liquid, and the gas (air) pressure is quite low compared with water pressure for unsaturated soils close to the ground surface.

Mixture coupling theory considers that the porous medium may deform, especially for large deformation of soft materials. A material point $\mathbf{X}^{\alpha}$ for the α th constituent in an arbitrary reference configuration will change to the position $\mathbf{x}^{\alpha}$ at time t, which can be defined as

$$\mathbf{x} = \mathbf{x}^{\alpha}(\mathbf{X}^{\alpha}, t) \tag{1}$$

Such definition also applies to β th matter.

V^{α} (V^{β})is defined as the volume of the α th constituent (β th matter)in V , V is the volume of the mixture, V^{pore} is the volume of the pore space and, therefore, the volume fraction of the β th matter, the porosity ϕ and the saturation of β th matter state (fluids only) are

$$\phi^{\beta}=\frac{V^{\beta}}{V},\ \phi=\frac{V^{pore}}{V},\ S^{\beta}=\frac{V^{\beta}}{V^{pore}} \tag{2}$$

The mass density can be defined in two different ways: ρ^{α} (ρ^{β})and ρ^{α}_{β} (ρ^{β}_{β}). ρ^{α} (ρ^{β}) is the mixture mass density of α th constituent (or the β th matter) relative to the volume of the whole mixture (V); ρ^{α}_{β} (ρ^{β}_{β}) is the matter state density of the α th constituent (or the β th matter) relative to the volume of the state of the mater V^{β} . For any constituents or matters in the mixture, the two densities relationship may be described as:

$$\rho^{\alpha}=\phi^{\beta}\rho^{\alpha}_{\beta},\ \rho^{\beta}=\phi^{\beta}\rho^{\beta}_{\beta} \tag{3}$$

where ϕ^{β} is the volume fraction of β th matter. For example, in a solid-liquid mixture with a chemical dissolved in the liquid (denote by subscript 'c'), the relationship of mixture density ρ^{l} and the state density ρ^{l}_{l}, and the mixture density of the chemical ρ^{c} and its corresponding state density ρ^{c}_{l} can be obtained as

$$\rho^{l}=\phi^{l}\rho^{l}_{l}=S^{l}\phi\rho^{l}_{l},\ \phi^{l}=S^{l}\phi,\ \rho^{c}=\phi^{l}\rho^{c}_{l}=S^{l}\phi\rho^{c}_{l} \tag{4}$$

where ϕ^{l} is the volume fraction of pore liquid, S^{l} is the saturation ratio of the liquid.

2.1 Balance equations for mass

The general balance laws for a thermodynamic open system may be described as [32-34]

$$\frac{D}{Dt}\left(\int_{V}\pi dV\right)=-\int_{S}\mathbf{I}_{\pi,ncon}\cdot\mathbf{n}dS-\int_{S}\mathbf{I}_{\pi,con}\cdot\mathbf{n}dS+\int_{V}r_{\pi}dV \tag{5}$$

where π denotes the bulk density of some extensive thermodynamic quantity (e.g. mass density, energy and so on), $\mathbf{I}_{\pi,con}$ and $\mathbf{I}_{\pi,ncon}$ are the convective flux and non-convective flux leave the region *V*, respectively, $\mathbf{n}$ is the outward unit normal vector on S , and r_{π} is a source term pertaining to the production of π .

In this research, it is assumed that there is no mass exchanges/reactions between constituents or point-mass sources, and the chemical constituents do not react. Then, the general mass balance law for the α-th constituent (also applies to the β th matter) can be obtained using equation (5) as [28]

$$\frac{D}{Dt}\int_V \rho^{\alpha} dV = -\int_S \rho^{\alpha}(\mathbf{v}^{\alpha} - \mathbf{v}^{s})\cdot \mathbf{n} dS \tag{6}$$

where ρ^{α} is the mass density of the α th constituent, $\mathbf{n}$ is the unit outward normal, $\mathbf{v}^{\alpha}$ is the velocity of the α th constituent, $\mathbf{v}^{s}$ is the velocity of the solid, and the time derivative following the motion of the solid is

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

where ∂_t is the time derivative and ∇ the gradient.

Equation (6) includes all types of constituents/matters. Multiphase fluids/chemicals in the porous medium (with consideration of the movement or deformation) can be obtained as

$$\frac{D}{Dt}\int_V \rho^{\alpha} dV = -\int_S \mathbf{I}^{\alpha}\cdot \mathbf{n} dS \tag{8}$$

where $\mathbf{I}^{\alpha}$ is the mass flux defined as

$$\mathbf{I}^{\alpha} = \rho^{\alpha}(\mathbf{v}^{\alpha} - \mathbf{v}^{s}) \tag{9}$$

For example, the liquid flux can be derived as

$$\mathbf{I}^{l} = \rho^{l}(\mathbf{v}^{l} - \mathbf{v}^{s})$$

The local balance equations of constituents can be derived by substituting equation (7) into equation (6), which leads to:

Solid mass:

$$\dot{\rho}^{s} + \rho^{s}\nabla\cdot\mathbf{v}^{s} = 0 \tag{10}$$

Water:

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

Chemicals:

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

in which the over dot '$\cdot$' is the time derivative ∂_t.

For the pore liquid containing water and chemics. The mass balance for the liquid as a whole can be rewritten as

$$\dot{\rho}^l + \rho^l \nabla \cdot \mathbf{v}^s + \nabla \cdot \mathbf{I}^l = 0 \tag{13}$$

in which there is relationship $\rho^l = \rho^w + \rho^c$ and $\mathbf{I}^l = \mathbf{I}^w + \mathbf{I}^c$.

2.2 Balance equation for energy

2.2.1 Heat

In the domain *V,* the thermal density changes only through the influx and efflux of thermal flow across the boundary *S* in the absence of chemical reaction. The thermal density of constituent α is

$$q^\alpha = \rho^\alpha C^\alpha T \tag{14}$$

In a mixture of solid and liquid (water and chemical), $q^s = \rho^s C^s T$ denotes the heat density of solids, $q^l = q^w + q^c = \rho^l C^l T$ denotes the heat density of liquid, C^s , C^l are the specific heat capacities of solid and liquid, respectively.

q^α in equation (14) is related to mass density ρ^α which is express relative to the mixture volume, similar to the mass density relationship, the thermo density can be relative to the matter state volume through

$$q^s = \phi^s q_s^s = \phi^s \rho_s^s C^s T \, , \; q^l = S^l \phi q_l^l = S^l \phi \rho_l^l C^l T \tag{15}$$

where $\phi^s = 1 - \phi$ is the volume fraction of the solid, ρ_s^s, q_s^s are the mass and heat density relative to the solid volume, q_l^l is the heat density of liquid relative to the liquid volume.

The total thermal flow $\mathbf{q}$ across the boundary *S* can be separated into two parts: 1) the heat flow contained in the liquid (e.g. water and chemical flow), which can be expressed as $h^w\mathbf{I}^w$ and $h^c\mathbf{I}^c$, in which h^w and h^c are the enthalpy of water and chemical, respectively; 2) the reduced heat flow $\mathbf{I}'_q = \mathbf{q} - h^w\mathbf{I}^w - h^c\mathbf{I}^c$, which is the difference between the total heat flow and the heat flow carried by the liquid [35]. Following the fundamental balance equation (5) for thermodynamically open systems, the heat balance equation can be derived as (neglecting point-heat source)

$$\frac{D}{Dt}\int_V (q^s + q^w + q^c)dV = -\int_S (\mathbf{I}'_q + h^w\mathbf{I}^w + h^c\mathbf{I}^c)\cdot\mathbf{n}dS \tag{16}$$

It is worth noting that the use of flow enthalpy to characterize flow heating influx and egress is valid only for quasi-equilibrium processes where there is no viscous/lost work done on the liquid and the pressure variation can be neglected, for any subvolume modelled.

Using equation (7), the equation (16) can be rewritten as

$$(q^s + q^w + q^c)^{\dot{}} + (q^s + q^w + q^c)\nabla\cdot\mathbf{v}^s + \nabla\cdot\mathbf{I}'_q + \nabla\cdot h^w\mathbf{I}^w + \nabla\cdot h^c\mathbf{I}^c = 0 \tag{17}$$

To simplify the discussion, the heat density of the mixture is expressed as $q^{mix} = q^s + q^w + q^c$, then equation (17) can be simplified as

$$\dot{q}^{mix} + q^{mix}\nabla\cdot\mathbf{v}^s + \nabla\cdot\mathbf{I}'_q + \nabla\cdot h^w\mathbf{I}^w + \nabla\cdot h^c\mathbf{I}^c = 0 \tag{18}$$

2.2.2 Helmholtz free energy

The Helmholtz free energy density can be obtained using the function $\psi = \varepsilon - T\eta$, where ε is the internal energy density and η *is the* entropy density[36]. The balance of internal energy is

$$\frac{D}{Dt}\int_V \varepsilon dV = \int_S (\boldsymbol{\sigma}\mathbf{v}^s - \mathbf{I}'_q)\cdot\mathbf{n}dS - \int_S (h^w\mathbf{I}^w + h^c\mathbf{I}^c)\cdot\mathbf{n}dS$$

and its local form as

$$\dot{\varepsilon} + \varepsilon \nabla \cdot \mathbf{v}^s - \nabla \cdot (\boldsymbol{\sigma} \mathbf{v}^s) + \nabla \cdot \mathbf{I}'_q + \nabla \cdot h^w \mathbf{I}^w + \nabla \cdot h^c \mathbf{I}^c = 0 \tag{19}$$

where $\boldsymbol{\sigma}$ is the Cauchy stress tensor.

Similar to equation (18), the balance of entropy for the mixture system is

$$\frac{D}{Dt}\int_V \eta^{mix} dV = -\int_S \mathbf{I}_\eta \cdot \mathbf{n} dS + \int_V \gamma dV$$

and its local form as

$$\dot{\eta}^{mix} + \eta^{mix} \nabla \cdot \mathbf{v}^s + \nabla \cdot \mathbf{I}_\eta - \gamma = 0 \tag{20}$$

in which

(1) η^{mix} is the entropy density of the mixture system described as

$$\eta^{mix} = \eta^s + \eta^w + \eta^c = \eta^s + \phi S^l \eta_l^w + \phi S^l \eta_l^c$$

and η^s, η^w, η^c are the entropy of the solid, water and chemical per unit mixture volume, η_l^w, η_l^c are the entropy of the water and chemical per unit liquid volume.

(2) $\mathbf{I}_\eta = \dfrac{\mathbf{q} - \mu^w \mathbf{I}^w - \mu^c \mathbf{I}^c}{T} = \dfrac{\mathbf{I}'_q}{T} + \eta^w \mathbf{I}^w + \eta^c \mathbf{I}^c$ is the entropy flux exchange with the surroundings [35] (the relationship $\mu^\alpha = h^\alpha - T\eta^\alpha$ is used);

(3) γ is the entropy produced per unit volume.

Assuming the temperature (*T*) is time-dependent only, from the definition of Helmholtz free energy density $\psi = \varepsilon - T\eta$, using material time derivative leads to the Helmholtz free energy density relationship in local form as

$$\dot{\psi} + \psi \nabla \cdot \mathbf{v}^s = \dot{\varepsilon} + \varepsilon \nabla \cdot \mathbf{v}^s - \dot{T}\eta - T\left(\dot{\eta} + \eta \nabla \cdot \mathbf{v}^s\right) \tag{21}$$

Then, from equations (19) and (20), the balance equation for free energy density is

$$\dot{\psi} + \psi \nabla \cdot \mathbf{v}^s - \nabla \cdot (\boldsymbol{\sigma} \mathbf{v}^s) + \nabla \cdot \mathbf{I}'_q + \nabla \cdot h^w \mathbf{I}^w + \nabla \cdot h^c \mathbf{I}^c + \dot{T}\eta^{mix} - T\nabla \cdot \mathbf{I}_\eta = -T\gamma \le 0 \tag{22}$$

3 Constitutive relations

Following the discussion of the balance equations in section 2, this section will establish the coupled relationship between the solid/liquid and the stress, strain and temperature response, using the dissipation function.

3.1 Coupling of water and thermal behaviour from entropy analysis

The transport process of liquid in the porous media will lead to frictional resistance at the solid and liquid interface, generating entropy production. A macroscopic expression for the dissipation is obtained by using standard arguments of non-equilibrium thermodynamics [12, 35]

$$T\gamma = -\mathbf{I}_{\eta} \cdot \nabla T - \mathbf{I}^{w} \cdot \nabla \mu^{w} - \mathbf{I}^{c} \cdot \nabla \mu^{c} \tag{23}$$

Equation (23) is different from the dissipation function under an isothermal condition because of the thermo related term $\mathbf{I}_{\eta}$ [12].

As pressure other than chemical potential is widely used in geotechnical engineering, it is necessary to build a relationship between chemical potential and pressure, which can be derived by using the Gibbs-Duhem equation[37] based on the assumption that the temperature influence on non-reactive chemical potential (e.g. water) can be ignored [38], leading to

$$\rho_{l}^{w} \nabla \mu^{w} + \rho_{l}^{c} \nabla \mu^{c} = \nabla p_{l} \tag{24}$$

in which p^{l} is the pore liquid pressure. Also, the Darcy velocity is defined through the definition [39]

$$\mathbf{u} = \phi^{l} (\mathbf{v}^{l} - \mathbf{v}^{s}) \tag{25}$$

where $\mathbf{v}^{l}$ is the barycentric velocity of the liquid which can be defined as

$$\mathbf{v}^{l} = \frac{\rho^{w}}{\rho^{l}} \mathbf{v}^{w} + \frac{\rho^{c}}{\rho^{l}} \mathbf{v}^{c}.$$

Hence, equations (15) and (16) can be used to rewrite the dissipation function as [12]

$$0 \le T\gamma = \mathbf{I}'_q \cdot \frac{\nabla(-T)}{T} - \mathbf{u}\nabla p_l - (\mathbf{J}^w \cdot \nabla\mu^w + \mathbf{J}^c \cdot \nabla\mu^c) \qquad (26)$$

where $\mathbf{J}^w = \mathbf{I}^w - \rho_l^w \mathbf{u}$, $\mathbf{J}^c = \mathbf{I}^c - \rho_l^c \mathbf{u}$ are the diffusion flux of the water and chemical. Using the phenomenological equation, the full coupling matrix can be written as [12]

$$\begin{pmatrix} \mathbf{u} \\ \mathbf{J}^c \\ \mathbf{I}'_q \end{pmatrix} = -\begin{bmatrix} \dfrac{k_{ef}}{v} & -\dfrac{k_{ef} r_l \rho_l^l}{v c^w} \dfrac{\partial\mu^w}{\partial c^c} & \dfrac{k_{ef} r_q \rho_l^l}{vT} \\ \dfrac{L\rho_l^l}{p_l} & \rho_l^l D & \dfrac{L_T}{T} \\ \dfrac{L_q \rho_l^l}{p_l} & \rho_l^l D_q & \lambda \end{bmatrix} \begin{pmatrix} \nabla p_l \\ \nabla c^c \\ \nabla T \end{pmatrix} \qquad (27)$$

where

- k_{ef} is the effective permeability and v is the fluid viscosity. Comparing to research on Darcy's law(e.g. [40, 41]), one could write $k_{ef} = kk_{rl}$, with k being the absolute permeability and k_{rl} being the relative permeability.
- r_l is the chemical reflection coefficient, which serves as a measure of the efficiency of the osmotic transport [42, 43].
- r_q is the thermal reflection coefficient, which serves as a measure of the efficiency of the osmotic transport. [11]
- L is the pressure diffusion coefficient for chemical transport.
- D is the dispersion-diffusion coefficient for chemical transport.
- c^c is the mass fraction of chemical c, c^w is the mass fraction of water.
- L_T is the thermal conduction coefficient for chemical transport.
- L_q is the pressure diffusion coefficient for thermal transport.
- D_q is the dispersion-diffusion coefficient for thermal transport.
- λ is the conduction coefficient.

It would be worth noting that from equation (26), It would be expected $\left(\mathbf{I}'_q, \mathbf{u}, \mathbf{J}^w, \mathbf{J}^c\right)^{\mathrm{T}}$ can be given by a matrix relationship with associate variables $\left(\nabla T, \nabla p_l, \mu^w, \mu^c\right)^{\mathrm{T}}$, these variables must be related in general in order to enforce equation (26). Assuming that $-\mathbf{J}^w \cdot \nabla\mu^w \ge 0$ always and the remainder of the inequality is still true, lead to a reduced form $\left(\mathbf{I}'_q, \mathbf{u}, \mathbf{J}^c\right)^{\mathrm{T}}$ with associate variables $\left(\nabla T, \nabla p_l, \mu^c\right)^{\mathrm{T}}$. Since the inputs and outputs of (27) are directional and the resulting form of (26) is not quadratic or otherwise constrained to be non-negative, verification of (26) stepwise is a requirement of any solution.

3.2 Basic equation of state

By assuming that the rock maintains mechanical equilibrium so that $\nabla \cdot \dot{\boldsymbol{\sigma}} = \mathbf{0}$, and combining equations (22) and (23), the resulting balance equation for ψ is derived as

$$\dot{\psi} + \psi \nabla \cdot \mathbf{v}^s - tr(\boldsymbol{\sigma} \nabla \mathbf{v}^s) + \mu^w \nabla \cdot \mathbf{I}^w + \mu^c \nabla \cdot \mathbf{I}^c + \eta^{mix} \dot{T} = 0 \qquad (28)$$

Equation (28) has included the temperature part $\eta^{mix}\dot{T}$ compared with previous work [28].

In order to obtain the expression of the referential equivalent of equation (28), the following classical continuum mechanics equations [10] will be needed.

$$\mathbf{F} = \frac{\partial \mathbf{x}^s}{\partial \mathbf{X}^s}(\mathbf{X}^s, t), \ \mathbf{E} = \frac{1}{2}(\mathbf{F}^{\mathbf{T}}\mathbf{F} - 1), \ \mathbf{T} = J\mathbf{F}^{-1}\boldsymbol{\sigma}\mathbf{F}^{-T}, \ J = \frac{dV}{dV_0}, \ \dot{J} = J\nabla \cdot \mathbf{v}^s \qquad (29)$$

where $\mathbf{F}$ is the solid deformation, $\mathbf{E}$ is the Green strain, $\mathbf{T}$ is the second Piola-Kirchhoff stress, J is the determinant of $\mathbf{F}$ which determine the volume change of the volume defined by the solid boundary, dV is the volume of a region bounded by solid in the current configuration, and dV_0 is the volume of the reference configuration bounded by the corresponding solid.

Using the continuum mechanics equation (29) and the mass balance equations (11), (12), the free energy in the reference configuration can be rewritten as

$$\dot{\Psi} = tr(\mathbf{T}\dot{\mathbf{E}}) + \mu^w \dot{m}^w + \mu^c \dot{m}^c - J\eta^{mix}\dot{T} \qquad (30)$$

where $\Psi = J\psi$ is the free energy in the reference configuration; $m^w = J\rho^w$ and $m^c = J\rho^c$ are the mass of the water and chemical per unit referential volume, respectively.

3.3 Helmholtz free energy density of the pore water and wetted mineral matrix

3.3.1 Pore liquid

If the Helmholtz free energy density of the pore fluid is ψ_{pore}, based on classical thermodynamics [35, 44], ψ_{pore} can be expressed as

$$\psi_{pore} = -p^{pore} + S^l \mu^c \rho_l^c + S^l \mu^w \rho_l^w \tag{31}$$

where p^{pore} is the pore pressure and it satisfies $p^{pore} \approx S^l p^l$, as the gas is ignored.

According to the Gibbs-Duhem equation for time derivative [35, 37]

$$\dot{p}^{pore} - S^l \eta_l^l \dot{T} = S^l \dot{\mu}^c \rho_l^c + S^l \dot{\mu}^w \rho_l^w \tag{32}$$

where η_l^l is the entropy of pore liquid per liquid volume.

Equation (32) can be arranged as $\dot{p}^{pore} = S^l \dot{\mu}^c \rho_l^c + S^l \dot{\mu}^w \rho_l^w + S^l \eta_l^l \dot{T}$. By substituting this equation into the time derivation of equation (31) as

$$\dot{\psi}_{pore} = -\dot{p}^{pore} + S^l \dot{\mu}^c \rho_l^c + S^l \dot{\mu}^w \rho_l^w + \mu^c (S^l \rho_l^c)^{\dot{}} + \mu^w (S^l \rho_l^w)^{\dot{}} \tag{33}$$

it leads to in a simplified $\dot{\psi}_{pore}$ as

$$\dot{\psi}_{pore} = -S^l \eta_l^l \dot{T} + \mu^c (S^l \rho_l^c)^{\dot{}} + \mu^w (S^l \rho_l^w)^{\dot{}} \tag{34}$$

3.3.2 Free energy density of the solid matrix

The free energy density of the solid matrix can be derived by subtracting the contribution of pore space $J\phi\psi_{pore}$ due to pore liquid from the total free energy Ψ of the combined rock/fluid system. The free energy density of the solid matrix is:

$$(\Psi - J\phi\psi_{pore})^{\dot{}} = \dot{\Psi} - \upsilon\dot{\psi}_{pore} - \psi_{pore}\dot{\upsilon} \tag{35}$$

where $\upsilon = J\phi$ is the pore volume per unit referential volume. By invoking equation (30) for $\dot{\Psi}$, (34) for $\dot{\psi}_{pore}$, and (31) for ψ_{pore} into equation (35), it leads to

$$\begin{aligned}(\Psi - J\phi\psi_{pore})^{\dot{}} &= \left[tr(\mathbf{T}\dot{\mathbf{E}}) + \mu^{w}\dot{m}^{w} + \mu^{c}\dot{m}^{c} - J\eta^{mix}\dot{T}\right] \\ &-\upsilon\left(-S^{l}\eta_{l}^{l}\dot{T} + \mu^{c}(S^{l}\rho_{l}^{c})^{\dot{}} + \mu^{w}(S^{l}\rho_{l}^{w})^{\dot{}}\right) - \left(-p^{pore} + S^{l}\mu^{c}\rho_{l}^{c} + S^{l}\mu^{w}\rho_{l}^{w}\right)\dot{\upsilon}\end{aligned} \tag{36}$$

Equation (36) can be rewritten as

$$\begin{aligned}(\Psi - J\phi\psi_{pore})^{\dot{}} &= \left[tr(\mathbf{T}\dot{\mathbf{E}}) + \mu^{w}\dot{m}^{w} + \mu^{c}\dot{m}^{c} - J\eta^{mix}\dot{T}\right] \\ &\quad + \dot{\upsilon}p^{pore} + \upsilon S^{l}\eta_{l}^{l}\dot{T} - \mu^{w}\left(\upsilon S^{l}\rho_{l}^{w}\right)^{\cdot} - \mu^{c}\left(\upsilon S^{l}\rho_{l}^{c}\right)^{\cdot}\end{aligned} \tag{37}$$

Since $J\eta^{mix} = J\eta^{s} + J\eta^{w} + J\eta^{c} = J\eta^{s} + J\phi S^{l}\eta_{l}^{w} + J\phi S^{l}\eta_{l}^{c}$, $\dot{m}^{w} = (J\rho^{w})^{\dot{}} = (\upsilon S^{f}\rho_{l}^{w})^{\dot{}}$, $\dot{m}^{c} = (J\rho^{c})^{\dot{}} = (\upsilon S^{f}\rho_{l}^{c})^{\dot{}}$, equation (37) can be simplified as

$$(\Psi - J\phi\psi_{pore})^{\dot{}} = tr(\mathbf{T}\dot{\mathbf{E}}) + p^{pore}\dot{\upsilon} - \mathrm{H}^{s}\dot{T} \tag{38}$$

where $\mathrm{H}^{s} = J\eta^{s} = J\eta^{mix} - J\phi S^{l}\eta_{l}^{w} - J\phi S^{l}\eta_{l}^{c}$ is the referential entropy density of the solid matrix.

4 Constitutive equations structure

For reasons of convenience, the dual potential (the solid deformation energy) is used as

$$W = (\Psi - J\phi\psi_{pore}) - p^{pore}\upsilon \qquad (39)$$

By substituting equation (38) into the time derivative of W, it satisfies the relationship

$$\dot{W}(\mathbf{E}, p^{pore}, T) = tr(\mathbf{T}\dot{\mathbf{E}}) - \upsilon\dot{p}^{pore} - \mathrm{H}^{s}\dot{T} \qquad (40)$$

which indicates that W is a function of $\mathbf{E}$, p^{pore} and T, and expressions for $\mathbf{T}$, υ and H^{s} may be obtained.

Since

$$\dot{W}(\mathbf{E}, p^{pore}, T) = \left(\frac{\partial W}{\partial E_{ij}}\right)_{p^{pore},T} \dot{E}_{ij} + \left(\frac{\partial W}{\partial p^{pore}}\right)_{E_{ij},T} \dot{p}^{pore} + \left(\frac{\partial W}{\partial T}\right)_{E_{ij},p^{pore}} \dot{T} \qquad (41)$$

the following equations are obtained:

$$T_{ij} = \left(\frac{\partial W}{\partial E_{ij}}\right)_{p^{pore},T}, \quad \upsilon = -\left(\frac{\partial W}{\partial p^{pore}}\right)_{E_{ij},T}, \quad \mathrm{H}^{s} = -\left(\frac{\partial W}{\partial T}\right)_{E_{ij},p^{pore}} \qquad (42)$$

If equation (42) is differentiated with respect to time, the fundamental constitutive equations for the evolution of stress, pore volume fraction and temperature can be expressed as

$$\dot{T}_{ij} = L_{ijkl}\dot{E}_{kl} - M_{ij}\dot{p}^{pore} - S_{ij}\dot{T} \qquad (43)$$

$$\dot{\upsilon} = M_{ij}\dot{E}_{ij} + Q\dot{p}^{pore} + B\dot{T} \qquad (44)$$

$$\dot{\mathrm{H}}^{s} = S_{ij}\dot{E}_{ij} + B\ \dot{p}^{pore} + Z\ \dot{T} \qquad (45)$$

where the parameters L_{ijkl}, M_{ij}, S_{ij}, Z, B and Q are material-dependent constants defined by the following group of equations

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

$$M_{ij} = -\left(\frac{\partial T_{ij}}{\partial p^{pore}}\right)_{E_{ij},T} = \left(\frac{\partial \upsilon}{\partial E_{ij}}\right)_{p^{pore},T},$$

$$S_{ij} = -\left(\frac{\partial T_{ij}}{\partial T}\right)_{E_{ij},p^{pore}} = \left(\frac{\partial \mathrm{H}^{s}}{\partial E_{ij}}\right)_{p^{pore},T} \tag{46}$$

$$Z = \left(\frac{\partial \mathrm{H}^{s}}{\partial T}\right)_{E_{ij},p^{pore}}, \; B = \left(\frac{\partial \upsilon}{\partial T}\right)_{E_{ij},p^{pore}} = \left(\frac{\partial \mathrm{H}^{s}}{\partial p^{pore}}\right)_{E_{ij},T}, \; Q = \left(\frac{\partial \upsilon}{\partial p^{pore}}\right)_{E_{ij},T}$$

Note: one example is provided for the derivation from equations (42) to (43):

Since $T_{ij} = \left(\frac{\partial W}{\partial E_{ij}}\right)_{p^{pore},T}$, using the differentiation chain rule leads to

$$\frac{\partial T_{ij}}{\partial t} = \frac{\partial}{\partial t}\left(\frac{\partial W}{\partial E_{ij}}\right)_{p^{pore},T} = \left(\frac{\partial}{\partial E_{ij}}\left(\frac{\partial W}{\partial t}\right)\right)_{p^{pore},T} = \left(\frac{\partial}{\partial E_{ij}}(\dot{W})\right)_{p^{pore},T} \tag{47}$$

Substituting equation (40) into equation (47) leads to

$$\frac{\partial T_{ij}}{\partial t} = \left(\frac{\partial}{\partial E_{ij}}(\dot{W})\right)_{p^{pore},T} = \left(\frac{\partial T_{ij}}{\partial E_{ij}}\right)_{p^{pore},T} \dot{E}_{kl} - \left(\frac{\partial \upsilon}{\partial E_{ij}}\right)_{p^{pore},T} \dot{p}^{pore} - \left(\frac{\partial \mathrm{H}^{s}}{\partial E_{ij}}\right)_{p^{pore},E_{kl}} \dot{T} \tag{48}$$

Comparing equation (48) with equation (43), the coefficients in equation (46) can be obtained as $L_{ijkl} = \left(\frac{\partial T_{ij}}{\partial E_{kl}}\right)_{p^{pore},T}$, $M_{ij} = \left(\frac{\partial \upsilon}{\partial E_{ij}}\right)_{p^{pore},T}$ and $S_{ij} = \left(\frac{\partial \mathrm{H}^{s}}{\partial E_{ij}}\right)_{p^{pore},T}$.

5 Final equations of motion for mixture coupling theory

5.1 Solids

The non-linearity of the equations is of a geometrical nature and associated with large deformations. For isotropic materials, the tensors M_{ij} and S_{ij} are diagonal; that is, they can be written in the form of scalars ζ and ω_T, as follows:

$$M_{ij} = \zeta\delta_{ij}\text{, } S_{ij} = \omega_T\delta_{ij} \tag{49}$$

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

$$L_{ijkl} = G(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + (K - \frac{2G}{3})\delta_{ij}\delta_{kl} \tag{50}$$

where G is the rock shear modulus and K the bulk modulus.

With the assumption of small strains, the governing stress (equation (43)) and pore fraction (equation (44)) equations can be changed to the form

$$\dot{\sigma}_{ij} = (K - \frac{2G}{3})\dot{\varepsilon}_{kk} + 2G\dot{\varepsilon}_{ij} - \zeta\,\dot{p}^{pore}\delta_{ij} - \omega_T\dot{T} \tag{51}$$

$$\dot{\upsilon} = \zeta\dot{\varepsilon}_{ii} + Q\dot{p}^{pore} + B\dot{T} \tag{52}$$

where $\varepsilon_{ij} = \frac{\partial d_i}{\partial x_j}$ and d_i is the displacement (*i*=1,2,3 or the vector $\mathbf{d} = [d_1, d_2, d_3]$); the void compressibility Q relates to the scalar ζ according to $Q = (1/K_s)(\zeta - \phi) + \phi^l / K_l$, in which K_s is the bulk modulus of the solid matrix and K_l is the bulk modulus of liquid mass; the quantity ζ is related to the bulk moduli, K and K_s, in a poroelastic manner, that is, $\zeta = 1 - (K / K_s)$; $\omega_T = K\beta_s$ with β_s being the thermal expansion coefficient of the solids, $B = -(\zeta - \phi)\beta_s$.

If the mechanical equilibrium condition ($\frac{\partial \dot{\sigma}_{ij}}{\partial x_j} = 0$) is introduced into equation (51), and by using the evolution of the pore pressure $\dot{p}^{pore}$ as [19]

$$\dot{p}^{pore} \approx \left(S^l p^l\right)^{\bullet} = (S^l + \frac{C_s^p}{\phi} p_l)\frac{\partial p_l}{\partial t} \tag{53}$$

where $C_s^p = \phi \frac{\partial S^l}{\partial p_l}$.

the final equation becomes

$$(K - \frac{2G}{3})\frac{\partial^2 \dot{d}_k}{\partial x_k \partial x_i} + G\left(\frac{\partial^2 \dot{d}_i}{\partial x_j \partial x_j} + \frac{\partial^2 \dot{d}_j}{\partial x_i \partial x_j}\right) - \zeta \nabla\left[(S^l + \frac{C_s^p}{\phi} p_l)\dot{p}_l\right] - \omega_T \frac{\partial \dot{T}}{\partial x_i} = 0 \tag{54}$$

5.2 Chemical potential and transport

5.2.1 Chemical potential

This section considers the case in which there are only two chemical components present: the solute (chemical) and diluent (water). The solute chemical potential is given by the expression[35]

$$\mu^c = g^c(p,T) + (\frac{RT}{M^c})(\ln a^c) \tag{55}$$

where g^c is a function that depends on pressure and temperature, and the term $(\frac{RT}{M^c})(\ln a^c)$ is the chemical activity-dependent term of μ^c. R, M^c and a^c are the gas constant, the molar mass and activity of the solute, respectively. Chemical activity is a measure of the ‘effective concentration’ of the solute in the mixture.

The relationship between a^c and x^c is

$$a^c = r_c x^c \tag{56}$$

where r_c is the activity coefficient. If the solution is assumed to be ideal, then $r_c = 1$, so that the solute activity a^c becomes equal to the solute mole fraction x^c. Note that the mole fraction x^c is related to the solute mass fraction c^c through

$$c^c = x^c M^c / (x^c M^c + (1 - x^c) M^w) \tag{57}$$

5.2.2 Chemical transport

From the balance equation (12) and the mass density relationship(4), using the Euler identity, for the α constituent ($\alpha = w, c$) in the liquid, there is

$$\overset{\cdot}{(S^l \upsilon \rho_l^\alpha)} + J\nabla \cdot (\rho^\alpha \mathbf{u}) + J\nabla \cdot \mathbf{J}^\alpha = 0 \tag{58}$$

By introducing the mass fraction $c^\alpha = \rho_l^\alpha / \rho_l^l$, equation (58) can be rearranged as

$$\overset{\cdot}{(S^l \upsilon \rho_l^l c^\alpha)} + \nabla \cdot (\rho_l^l c^\alpha \mathbf{u}) + J\nabla \cdot \mathbf{J}^\alpha = 0 \tag{59}$$

Because $\sum_\alpha c^\alpha = 1$ and $\sum_\alpha \mathbf{J}^\alpha = 0$, summing over all the fluid components leads to the relationship

$$\overset{\cdot}{(\upsilon S^l \rho_l^l)} + J\nabla \cdot (\rho_l^l \mathbf{u}) = 0 \tag{60}$$

By invoking equation(60), equation (58) can be transformed to

$$\upsilon S^l \rho_l^l \dot{c}^\alpha + J\rho_l^l \mathbf{u} \cdot \nabla c^\alpha + J\nabla \cdot \mathbf{J}^\alpha = 0 \tag{61}$$

By substituting equation (27) into equation (61) and using the chemical potential relationship (55) and the relevant derivation in reference [1], the chemical transport equation can be derived as

$$\begin{aligned} &\upsilon S^l \rho_l^l \dot{c}^c - J\rho_l^l k \frac{k_{rl}}{v} \left(\nabla p^l - r_l \rho_l^l \frac{1}{c^w c^c} \frac{RT}{M^c} \nabla c^c + \frac{r_q \rho_l^l}{T} \nabla T \right) \cdot \nabla c^c \\ &+ J\nabla \cdot \left[-\frac{L\rho_l^l}{p^l} \nabla p^l - \rho_l^l D \nabla c^c - \nabla T \right] = 0 \end{aligned} \tag{62}$$

In this equation, the chemical and thermal osmosis influence, as well as the pressure and temperature influence on diffusion, have been embedded. Without considering such thermal coupled influence, the equation will become the same equation as chemical osmosis [2].

5.3 Hydraulic

From equations (4) and (13), and using the Euler identity, the following equation is derived

$$\dot{\overline{(\upsilon S^l \rho_l^l)}} + J\nabla\cdot(\rho_l^l \mathbf{u}) = 0 \tag{63}$$

Expand the first term in equation (63), it leads to

$$S^l \rho_l^l \dot{\upsilon} + \upsilon \rho_l^l \dot{S}^l + \upsilon S^l \dot{\rho}_l^l + J\nabla\cdot(\rho_l^l \mathbf{u}) = 0 \tag{64}$$

With equations (52) and (27), the control equation for the liquid transport can be written as

$$\begin{aligned} & S^l \rho_l^l \zeta \nabla\cdot\dot{\mathbf{d}} + S^l \rho_l^l Q \dot{p}^{pore} + S^l \rho_l^l B \dot{T} + \upsilon \rho_l^l \dot{S}^l + \upsilon S^l \dot{\rho}_l^l \\ & + J\nabla\cdot\left[-\rho_l^l k \frac{k_{rl}}{v}\left(k \frac{k_{rl}}{v}\nabla p_l - r_l \rho_l^l \frac{1}{c^w c^c}\frac{RT}{M^c}\nabla c^c + \frac{r_q \rho_l^l}{T}\nabla T\right)\right] = 0 \end{aligned} \tag{65}$$

Considering the average pressure definition in equation (53), alongside the rate of saturation as a function of pressure $S^l = S^l(p^l)$ and the water density as a function of pressure and density $\rho_l^l = \rho_l^l\left(p^l, T\right)$ [19, 45, 46] as

$$\begin{aligned} \dot{S}^l(p^l) &= \frac{\partial S^l}{\partial p^l}\frac{\partial p^l}{\partial t} = \frac{C_s^p}{\upsilon}\frac{\partial p^l}{\partial t} \\ \dot{\rho}_l^l(T, p^l) &= \rho_l^l\left(\frac{1}{K_l}\dot{p}^l - \beta_l \dot{T}\right) \end{aligned} \tag{66}$$

where K_l is the bulk modulus of the liquid with $\frac{1}{K_l} = \frac{1}{\rho_l^l}\left(\frac{\partial \rho_l^l}{\partial p^l}\right)_T$, β_l is the thermo expansion coefficient of the liquid with $\beta_l = -\frac{1}{\rho_l^l}\left(\frac{\partial \rho_l^l}{\partial T}\right)_{p^l}$.

With equation (66) and relationship (53), and neglecting the space variation of liquid density, e.g. $\nabla \rho_l^l = 0$, equation (65) can then be rewritten as

$$\begin{aligned} & S^{l}\zeta\nabla\cdot\dot{\mathbf{d}}+\left[S^{l}Q\left(\frac{C_{s}^{p}}{\phi}+S^{l}\right)+\left(C_{s}^{p}+\frac{\upsilon S^{l}}{K_{l}}\right)\right]\frac{\partial p^{l}}{\partial t}+S^{l}\left(B-\upsilon\beta_{l}\right)\dot{T} \\ & -J\nabla\cdot k\frac{k_{rl}}{v}\left(\nabla p^{l}-r_{l}\rho_{l}^{l}\frac{1}{c^{w}c^{c}}\frac{RT}{M^{c}}\nabla c^{c}+\frac{r_{q}\rho_{l}^{l}}{T}\nabla T\right)=0 \end{aligned} \tag{67}$$

Note: The mass density of water in the “liquid” volume also changes, even if the volume change is negligible.

5.4 Thermo transport

From equation(15), by using Euler identity, equation (17) can be rewritten as

$$(\upsilon^{s}\rho_{s}^{s}C^{s}T+S^{l}\upsilon q_{l}^{l}C^{l}T)^{\boldsymbol{\cdot}}+J\nabla\cdot\mathbf{I}'_{q}+J\nabla\cdot h^{l}\mathbf{I}^{l}=0 \tag{68}$$

Where $\upsilon^{s}=J\phi^{s}=1-\upsilon$ is the solid mass fraction in the reference configuration.

From the flux equation (9), density relationship (4)and Darcy velocity (25), the heat fluid carried by the liquid can be written as

$$h^{l}\mathbf{I}^{l}=C^{l}T\rho_{l}^{l}\mathbf{u} \tag{69}$$

in which the expression $h^{l}\mathbf{I}^{l}=C^{l}T\rho_{l}^{l}\mathbf{u}$ is adopted.

Since the attention of this paper is to focus on the coupled chemical and thermal osmosis, by neglecting the temperature and pressure dependence of fluid and solid densities and neglecting the thermal coupling term due to pressure or chemical, equation (68) can be rearranged as

$$\frac{\partial}{\partial t}\left\{\left[(1-\upsilon)\rho_{s}^{s}C^{s}+\upsilon S^{l}\rho_{l}^{l}C^{l}\right]T\right\}-J\nabla^{T}\lambda\nabla T+J\nabla\cdot C^{l}T\rho_{l}^{l}\mathbf{u}=0 \tag{70}$$

which is the same function as that derived based on the mechanics approach [19].

5.5 Validation and innovation of the constitutive equations

The mechanical deformation equation (54) has a similar formulation to the deformation equation presented in [11], however, the liquid pressure variation p_l accounts for the combined influence of chemical and thermal osmosis in the equation in section 5.3, which therefore is a further extension from the current state-of-the-art understanding. The fluid transport equation (67) has extended previous published equations [1, 2] by considering the chemical osmosis influence, by incorporating the thermal influence term $\frac{r_q \rho_l^l}{T} \nabla T$. The same heat transport equation (70) [16] has been obtained purely through the mathematical derivations after simplification of equation (70).

6 Numerical results for coupled thermal and chemical osmosis

This section focuses on the influence of coupled chemical osmosis and thermal osmosis induced flow, and their consequent influence on THMC processes. The governing equations (54) , (62), (67), (70) are solved by using the classic finite element method [19] for variables of the displacement vector $\mathbf{d}$, liquid pressure p^l , chemical concentration c^c , and temperature T .

A simple numerical model has been established to simulate the mechanical behaviour of an unsaturated very-low permeability rock formation (Fig 1).

6.1 Geometry and boundary conditions

Fig 1 shows the geometry and boundary conditions of model domain. Boundary A is free and permeable and boundary B is fixed and impermeable. The upper and lower boundary are on rollers allowing only horizontal displacement.

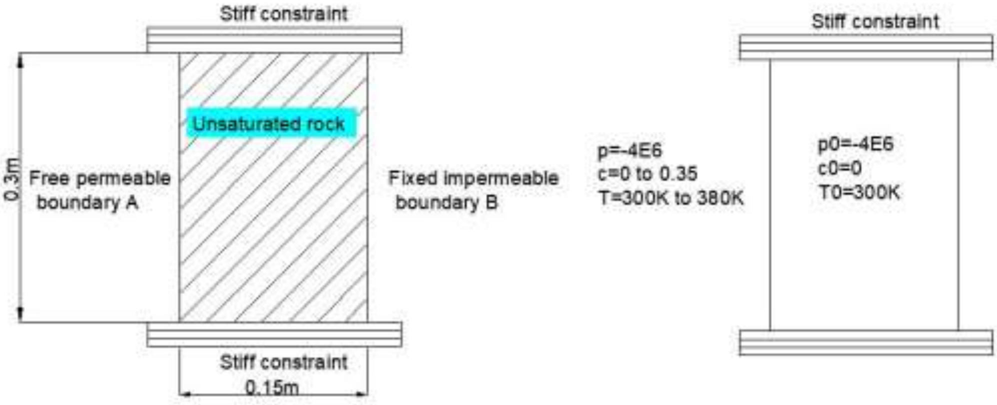

Fig 1. Geometry and boundary conditions.

As this numerical simulation focuses on chemical and thermal osmosis, no pressure gradient is applied. At boundary A, the pressure is set at -4 MPa and remains constant during the modelling process. The domain is assumed to contain water at a pressure of

-4 MPa with the saturation of 0.9951 by adopting the Van Genuchten relationship [47], which is used to define the relative permeability and saturation as

$$k_{rl} = \left(S^l\right)^{0.5}\left[1-\left(1-\left(S^l\right)^{1/m}\right)^m\right]^2$$

$$S^l = \left[\left(-p^l / M\right)^{1/(1-m)} + 1\right]^{-m}$$

The initial mass fraction of the chemical in the domain is set to be zero. At boundary A, the mass fraction (chemical) rises from 0 to 0.35 to simulate the chemical gradient. The initial mass fraction at boundary B is 0, but not fixed. The initial temperature is set to be 300 K across the domain, and rises to 380 K on boundary A (t>0).

Parameters adopted in this numerical simulation are listed in Table 1.

Table 1. Material parameters [48].

Parameters	Physical meaning	Values and units
ρ_l^l	Density of fluid	1113 kg/m^3
ϕ	Porosity	0.1
k	permeability	1 mD
θ	Dynamic viscosity	3e-4 Pa*s
m	van Genuchten parameter	0.43
M	van Genuchten parameter	51 MPa
E	Young's modulus	24.14 GPa
ν	Poisson's ratio	0.3
ζ	Biot's coefficient	1
C^w	Specific heat of fluid	4181 J/Kg/K
C^s	Specific heat of solid	768 J/Kg/K
r_q	Thermal reflection coefficient	1 (assumed)
r_l	Chemical reflection	0.003 [49]
D	Diffusion coefficient	5e-9 m^2/s

6.2 Numerical results

6.2.1 THMC coupling

The classic finite element method [19, 50] has been used to solve the governing equations. Fig 2 shows the chemical mass fraction change with time. As the chemical mass fraction rises from 0 to 0.35 at boundary A, the chemical species transports from high mass fraction to low mass fraction. As a result, mass fraction in the domain increases with time. At t = 7.2e5 s (200 h), the mass fraction reaches a stable state. After that, the chemical mass fraction remains constant.

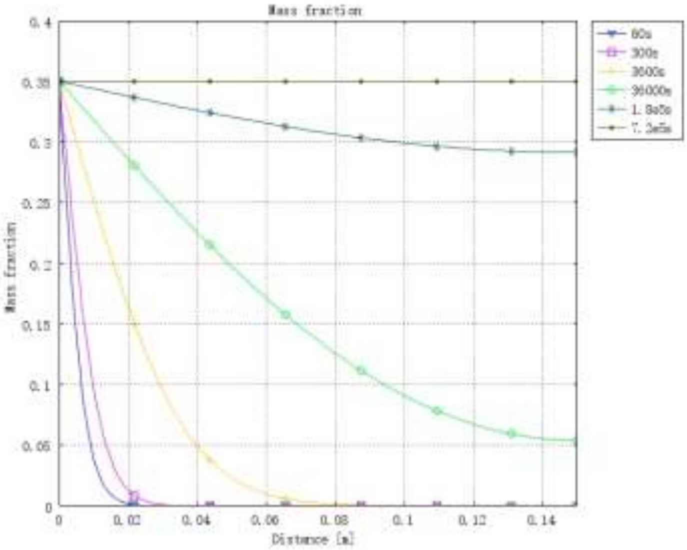

Fig 2. Evolution of chemical mass fraction distribution with time.

Fig 3 shows the temperature change with time. The trend of temperature change is very similar to the trend of chemical mass fraction change. The difference is that temperature changes at a much faster rate than chemical mass fraction change [51]. At t = 1.8e5 s (50 h), the temperature has reached a stable state whereas the chemical mass fraction is still changing.

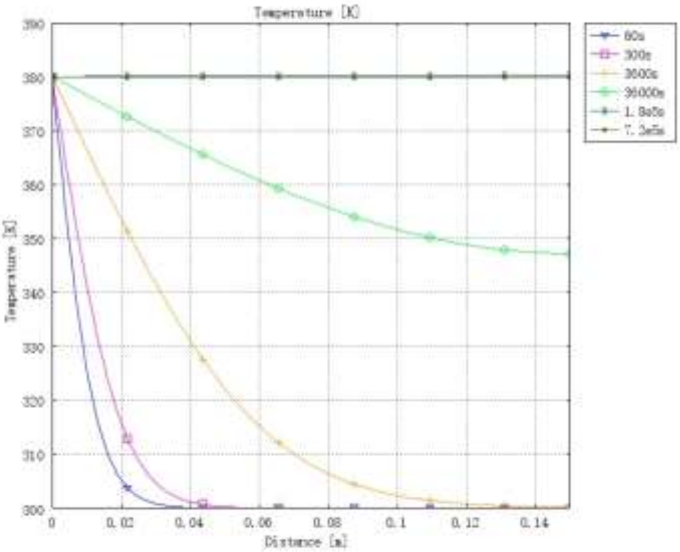

Fig 3. Evolution of Temperature distribution with time.

Figs 4-6 show the evolution of pressure, saturation and displacement with time under the influence of chemical osmosis and thermal osmosis. Pressure in the domain is significantly changed by chemical and thermal osmosis. As saturation and pressure are linked by the van Genuchten relationship, the trend of saturation distribution is very similar to the trend of pressure.

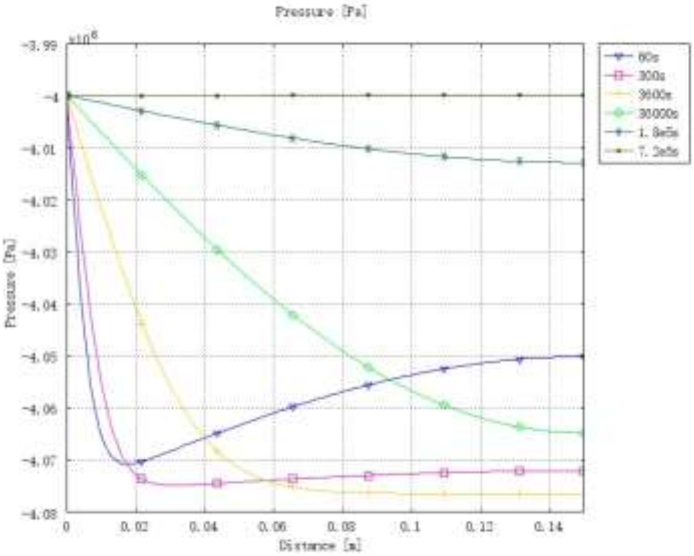

Fig 4. Pressure change induced by chemical osmosis and thermal osmosis.

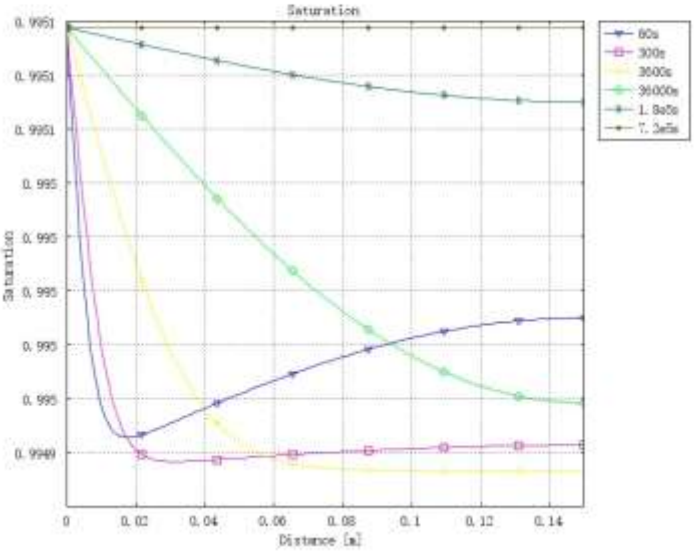

Fig 5. Saturation change induced by chemical osmosis and thermal osmosis.

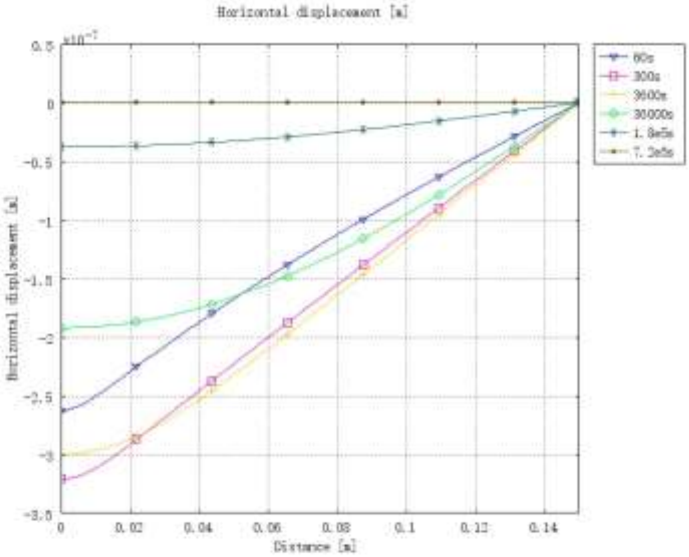

Fig 6. Horizontal displacement induced by chemical osmosis and thermal osmosis.

6.2.1 chemical or thermal osmosis

By setting the thermal reflection coefficient $r_q = 1$ with the chemical reflection coefficient set to $r_l = 0$, or by setting the thermal reflection coefficient $r_q = 0$ with the chemical reflection coefficient set to $r_l = 0.003$, the pressure change with time under the influence of chemical osmosis only or thermal osmosis only can be obtained (Fig 7 and Fig 8), respectively.

Fig 7 shows the chemical osmosis influence on water pressure. Due to a chemical gradient between boundary A and the domain, water will flow out from the domain via boundary A, leading to the reduction of saturation (Fig 9) and a corresponding reduction of the pore water pressure (Fig 7). At the early stage of this simulation (e.g. 60 s, 300 s), as the chemical gradient near boundary A is larger, the water loss near boundary A is quicker than that near boundary B. As a result, the pressure and saturation change near boundary A is more significant (note: pressure at boundary A is constant). As the chemical gradient dissipates along with time, water flows back into boundary A and gradually covers the whole domain, and the water pressure at boundary B recovers from the lowest (e.g. at t=3600s) to the original -4MPa.

Figure 8 shows the pressure change caused by thermal osmosis only. Compared with the chemical osmosis process (Figs 7 and 9), one of the major differences is that the thermal osmosis flow direction is opposite to the chemical osmosis flow direction, hence, the water pressure does not decrease but increases.

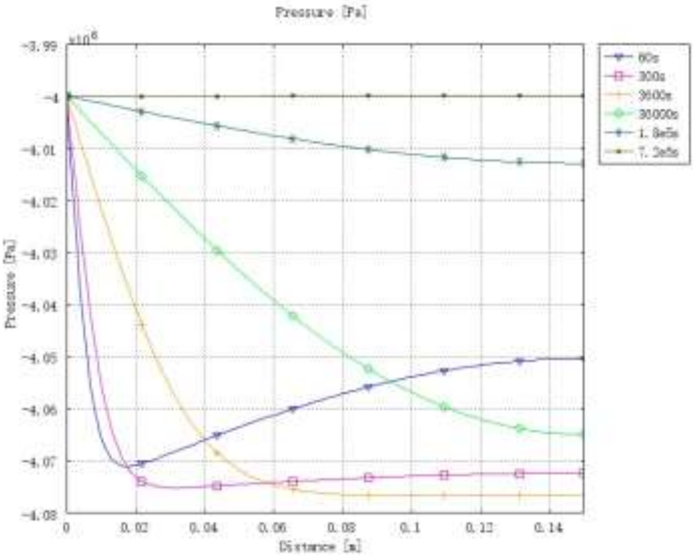

Fig 7. Pressure change induced by chemical osmosis.

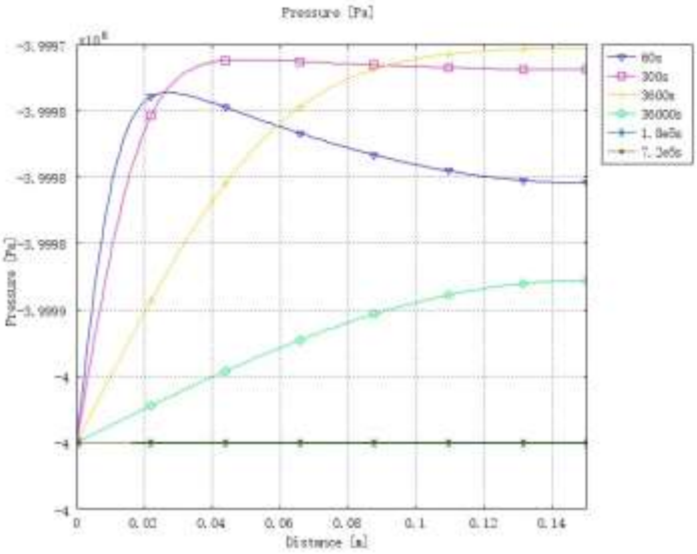

Fig 8. Pressure change induced by thermal osmosis.

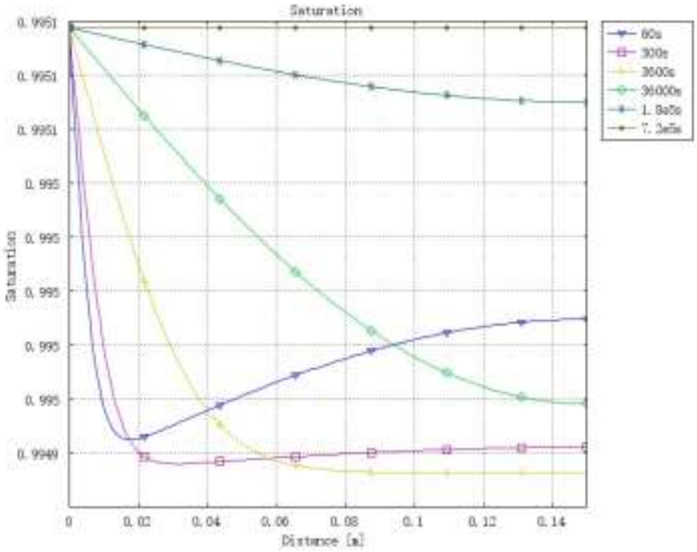

Fig 9. Saturation change induced by chemical osmosis.

Comparing Fig 7 and Fig 8, the pressure change caused by chemical osmosis is significantly bigger than that caused by thermal osmosis under the simulation conditions considered ($r_q = 1, r_l = 0;\ r_l = 0.003, r_q = 0$). As water pressure change section 6.2.1 (THMC) is the combined influence of chemical osmosis and thermal osmosis, Fig 4 is very similar to Fig 7. For the same reason, Fig 9 and Fig 5 are very similar.

Since the flow direction of thermo osmosis can be either from high temperature to low temperature, or vice versa [8], the thermal reflection coefficient is set to be $r_q = -1$ ($r_l = 0$)

to compare with $r_q = 1$ $(r_l = 0)$. The resulting pressure changes are presented in Fig 11: if $r_q = 1$, the pressure increases. Whereas, if $r_q = -1$, the pressure decreases.

Similarly, by setting the chemical reflection coefficient $r_l = 0.003$ or $r_l = -0.003$ ($r_q=0$), the pressure changes caused by chemical osmosis (positive and negative) are obtained, as shown in Fig 11: Pressure changes are observed with opposing trends under the opposite (e.g. + or -) chemical reflection coefficients.

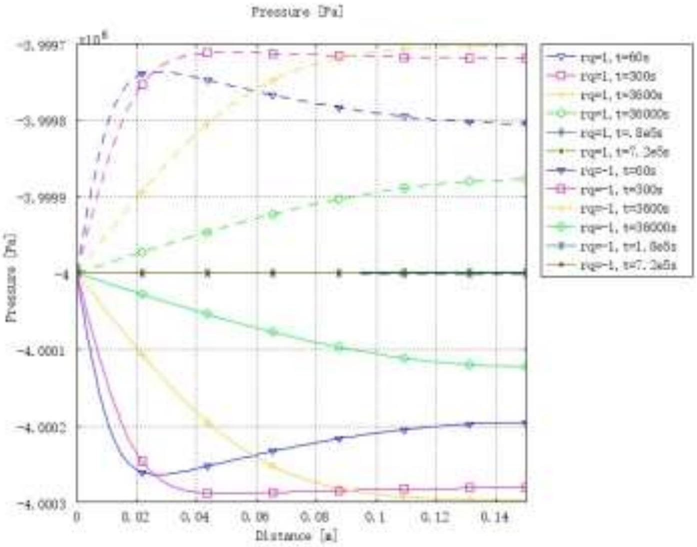

Fig 10. Pressure change induced by thermal osmosis (rq=1& rq=-1).

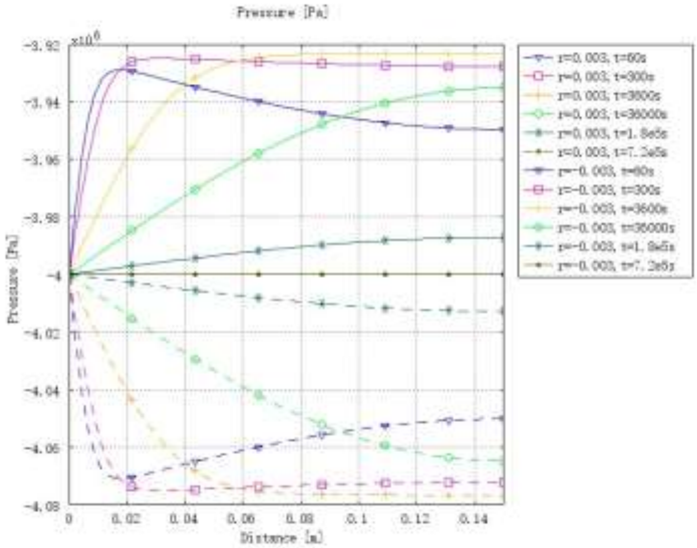

Fig 11. Pressure change induced by chemical osmosis (r=0.003& rq=-0.003).

7 Conclusion

In this paper, a new THMC model has been presented incorporating coupled chemical osmosis and thermal osmosis based on mixture coupling theory. Classic Darcy's law has been extended considering the respective osmotic flux components. The numerical model has illustrated the influence of chemical osmosis and thermal osmosis on the mechanical behaviour of unsaturated rock. Chemical osmosis and thermal osmosis have both been found to induce fluid flux movement and alter the pressure distribution in the domain under the conditions considered in this work. Further experiments might be required to identify the parameters in greater detail. As the result is a combined influence of chemical osmosis and thermal osmosis, it points out a potential to change one process to reduce/enlarge the influence of the other.

Acknowledgements

The first author acknowledges the CERES studentship from the university of Leeds, the second author acknowledges the financial support by a University of Leeds Research Grant (40711500). The third and fifth authors acknowledge the financial support by the Welsh European Funding Office (WEFO) through the FLEXIS project.

References

[1] X. Chen, M.A. Hicks, Unsaturated hydro-mechanical-chemo coupled constitutive model with consideration of osmotic flow, Comput Geotech, 54 (2013) 94-103.
[2] X. Chen, W. Pao, S. Thornton, J. Small, Unsaturated hydro-mechanical–chemical constitutive coupled model based on mixture coupling theory: Hydration swelling and chemical osmosis, International Journal of Engineering Science, 104 (2016) 97-109.
[3] A. Ghassemi, A. Diek, Linear chemo-poroelasticity for swelling shales: theory and application, Journal of Petroleum Science and Engineering, 38 (2003) 199-212.
[4] R. Schlemmer, J.E. Friedheim, F.B. Growcock, J.B. Bloys, J.A. Headley, S.C. Polnaszek, Chemical osmosis, shale, and drilling fluids, Spe Drilling & Completion, 18 (2003) 318-331.
[5] N. Ghaffour, T.M. Missimer, G.L. Amy, Technical review and evaluation of the economics of water desalination: Current and future challenges for better water supply sustainability, Desalination, 309 (2013) 197-207.
[6] C. Dirksen, Thermo-Osmosis Through Compacted Saturated Clay Membranes1, Soil Science Society of America Journal, 33 (1969) 821-826.

[7] R. Srivastava, P. Avasthi, Non-equilibrium thermodynamics of thermo-osmosis of water through kaolinite, J Hydrol, 24 (1975) 111-120.
[8] J. Goncalves, G. de Marsily, J. Tremosa, Importance of thermo-osmosis for fluid flow and transport in clay formations hosting a nuclear waste repository, Earth and Planetary Science Letters, 339 (2012) 1-10.
[9] S. Kim, M.M. Mench, Investigation of temperature-driven water transport in polymer electrolyte fuel cell: Thermo-osmosis in membranes, Journal of Membrane Science, 328 (2009) 113-120.
[10] X. Chen, M.A. Hicks, A constitutive model based on modified mixture theory for unsaturated rocks, Comput Geotech, 38 (2011) 925-933.
[11] X. Chen, W. Pao, X. Li, Coupled thermo-hydro-mechanical model with consideration of thermal-osmosis based on modified mixture theory, Int J Eng Sci, 64 (2013) 1-13.
[12] X. Chen, M. Wang, M.A. Hicks, H.R. Thomas, A new matrix for multiphase couplings in a membrane porous medium, Int J Numer Anal Methods Geomech, (2018).
[13] K. Terzaghi, Theory of consolidation, Theoretical Soil Mechanics, (1943) 265-296.
[14] M.A. Biot, Mechanics of deformation and acoustic propagation in porous media, Journal of applied physics, 33 (1962) 1482-1498.
[15] M.A. Biot, G. Temple, Theory of finite deformations of porous solids, Indiana University Mathematics Journal, 21 (1972) 597-620.
[16] S. Seetharam, H. Thomas, P.J. Cleall, Coupled thermo/hydro/chemical/mechanical model for unsaturated soils—Numerical algorithm, International Journal for Numerical Methods in Engineering, 70 (2007) 1480-1511.
[17] J. Huyghe, J. Janssen, Thermo-chemo-electro-mechanical formulation of saturated charged porous solids, Transport in Porous Media, 34 (1999) 129-141.
[18] A. Graziani, D. Boldini, Influence of hydro-mechanical coupling on tunnel response in clays, J Geotech Geoenviron Eng, 138 (2011) 415-418.
[19] R.W. Lewis, B.A. Schrefler, The finite-element method in deformation and consolidation of porous media, Wiley, New York, 1987.
[20] C. Truesdell, Sulle basi della termomeccanica, Rend. Lincei, 22 (1957) 33-38.
[21] R.M. Bowen, Diffusion models implied by the theory of mixtures, in: Rational thermodynamics, Springer, 1984, pp. 237-263.
[22] R.M. Bowen, Incompressible Porous-Media Models by Use of the Theory of Mixtures, Int J Eng Sci, 18 (1980) 1129-1148.
[23] K.R. Rajagopal, L. Tao, Mechanics of mixtures, World scientific, 1995.
[24] K. Rajagopal, L. Tao, On the propagation of waves through porous solids, International Journal of Non-Linear Mechanics, 40 (2005) 373-380.
[25] K. Rajagopal, On a hierarchy of approximate models for flows of incompressible fluids through porous solids, Mathematical Models and Methods in Applied Sciences, 17 (2007) 215-252.
[26] W. Heidug, S.W. Wong, Hydration swelling of water - absorbing rocks: a constitutive model, Int J Numer Anal Methods Geomech, 20 (1996) 403-430.
[27] X. Chen, Unsaturated hydro-chemo-mechanical modelling based on modified mixture theory, in: Faculty of Engineering and Physical Sciences, University of Manchester 2010.
[28] X. Chen, Constitutive unsaturated hydro-mechanical model based on modified mixture theory with consideration of hydration swelling, International Journal of Solids and Structures, 50 (2013) 3266-3273.
[29] W. Chen, X. Tan, H. Yu, G. Wu, S. Jia, A fully coupled thermo-hydro-mechanical model for unsaturated porous media, J Rock Mech Geotech Eng, 1 (2009) 31-40.

[30] N.M. Safai, G.F. Pinder, Vertical and horizontal land deformation in a desaturating porous medium, Adv. Water Res., 2 (1979) 19-25.
[31] S.P. Neuman, Galerkin approach to saturated–unsaturated flow in porous media, in: R.H. Gallagher, J.T. Oden, C. Taylor, O.C. Zienkiewicz (Eds.) Finite Elements in Fluids, John Wiley & Sons, New York, 1975.
[32] C. Truesdell, R. Toupin, The classical field theories, in: S. Flügge (Ed.) Handbuch der Physik Springer-Verlag, Berlin, 1960, pp. 226-793.
[33] D. Kondepudi, Introduction to modern thermodynamics, Wiley, 2008.
[34] S.I. Sandler, Chemical, biochemical, and engineering thermodynamics, John Wiley & Sons, 2017.
[35] A. Katchalsky, P.F. Curran, Nonequilibrium thermodynamics in biophysics, Harvard University Press, Cambridge, MA, 1965.
[36] Hasse.R, Thermodynamics of irreversible processes, Addison Wesley 1969.
[37] M.J. Moran, H.N. Shapiro, D.D. Boettner, M.B. Bailey, Fundamentals of engineering thermodynamics, John Wiley & Sons, 2010.
[38] X.H. Chen, M.A., Extending of Darcy's Law for Thermo Hydro Mechanical Chemo Coupling, in: Presentation in Alert Geomaterials, France, 2008.
[39] H. Darcy, Les fontaines publiques de la ville de Dijon: exposition et application, Victor Dalmont, 1856.
[40] C.W. Botermans, D.W. van Batenburg, J. Bruining, Relative permeability modifiers: Myth or reality?, in: SPE European Formation Damage Conference, OnePetro, 2001.
[41] M. Honarpour, S. Mahmood, Relative-permeability measurements: An overview, Journal of petroleum technology, 40 (1988) 963-966.
[42] W.K. Heidug, S.W. Wong, Hydration swelling of water-absorbing rocks: A constitutive model, Int. J. Num. Anal. Meth. Geomech., 20 (1996) 403-430.
[43] A. Staverman, The theory of measurement of osmotic pressure, Recueil des Travaux Chimiques des Pays-Bas, 70 (1951) 344-352.
[44] H.C. Van Ness, Understanding Thermodynamics, Dover Publications, New York, 1969.
[45] R. Nair, Y. Abousleiman, M. Zaman, A finite element porothermoelastic model for dual - porosity media, Int J Numer Anal Methods Geomech, 28 (2004) 875-898.
[46] L.J. Hosking, M. Chen, H.R. Thomas, Numerical analysis of dual porosity coupled thermo-hydro-mechanical behaviour during CO2 sequestration in coal, International Journal of Rock Mechanics and Mining Sciences, 135 (2020) 104473.
[47] M.T. van Genuchten, A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, Soil Science Society of America J., 44 (1980) 892-898.
[48] M.F. Kanfar, Z. Chen, S.S. Rahman, Analyzing wellbore stability in chemically-active anisotropic formations under thermal, hydraulic, mechanical and chemical loadings, Journal of Natural Gas Science and Engineering, 41 (2017) 93-111.
[49] T.J.S. Keijzer, P.J. Kleingeld, J.P.G. Loch, Chemical osmosis in compacted clayey material and the prediction of water transport, Engineering Geology, 53 (1999) 151-159.
[50] I.M. Smith, D.V. Griffiths, L. Margetts, Programming the finite element method, John Wiley & Sons, 2013.
[51] A. Gens, L.d.N. Guimarães, A.M. Fernández, M. Sánchez, S. Olivella, Formulation for the THMC analysis of clayey materials: application to radioactive waste disposal, in: GeoCongress 2008: Characterization, Monitoring, and Modeling of GeoSystems, 2008, pp. 1053-1060.