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Mathematical Model of Coupled Dual Chemical Osmosis Based on Mixture-Coupling Theory

Xiaohui Chen[1*], Steven F. Thornton[2], William Pao[3]

[*1]School of Civil Engineering, University of Leeds, UK

[*]Telephone: +44 (0)113 3430350

[*]Email: x.chen@leeds.ac.uk

[2]Groundwater Protection and Restoration Group, Dept of Civil and Structural Engineering, The University of Sheffield

[3]Mechanical Engineering Department, Universiti Teknologi PETRONAS, Block 17.03.10, Bandar Seri Iskandar, 31750 Tronoh, Perak Darul Ridzuan, Malaysia

ABSTRACT

Very low permeability soils and rocks can act as a semi-permeable osmotic membrane, which will generate osmotic flow. Such complexities have been extensively studied, but dual chemical osmosis, the influence of sorption on chemical osmotic flow and the consequent influence on the stress/stain change remains unclear. This study extends mixture-coupling theory, by including chemical sorption entropy and chemical potential, and provides a new-coupled formulation for chemical transport in very low permeability rock. The classical Darcy's Law and Fick's Law have been modified to include the influence of chemical potential and sorption under relevant conditions, and dual chemical osmosis. The mechanical deformation has been coupled with the water and chemical flows using Helmholtz free energy. Finally, a coupled unsaturated hydro-mechanical-chemical model which considers dual chemical osmosis and sorption is presented. This mathematical model provides the possibility of using dual chemicals to control osmotic flow and chemical transport, which leads to important engineering applications such as those in the field of nuclear waste disposal.

Keywords: Porous Media, Mixture Coupling Theory, Coupled modelling, Chemical Osmosis, Groundwater

1 INTRODUCTION

Chemical osmosis is an important process in very low permeability soils and rocks when the hydraulic conductivity is less than 10^{-10} m/s [1]. Such soils and rocks can act as semi-permeable membranes and restrict the migration of large solute molecules. Solutes in the subsurface, which are influenced by this process, originate from a diverse range of sources and industrial applications, including carbon geological storage and nuclear waste disposal. Single chemical osmosis has been studied within nuclear waste disposal and Darcy's Law has been extended accordingly [2, 3]. However, dual coupled chemical osmosis, the influence of sorption, and its subsequent effect on solid consolidation has not received any attention. This knowledge is important because it provides a deeper understanding of chemical transport in very low permeability porous media; a better prediction of chemicals transport with consideration of molecular-coupling of dual chemicals, and most importantly it potentially offers a new method to control specific chemicals (e.g. radionuclides) by using another non-harmful chemical.

Several approaches have been developed to model the coupling between thermo-hydro-mechanical-chemical components. These comprise : (1) mechanics approach, based on classical consolidation theories of Terzaghi [4] and Biot [5, 6], in which considerable research has been done, including the development of hydro-mechanical coupled models , and theoretical analysis of thermal and/or chemo coupling [7, 8]; (2) mixture theory approach, which was firstly developed by Truesdell [9] and further extended by Bowen [10-12], maintains the individuality of the solid and fluid phases [12, 13], with recent contribution by Rajagopal etc. [14-18]. A comprehensive review of this approach has been completed by Atkin and Craine [19]. This approach has the difficulties of obtaining information on the interaction between the phases as discussed by Rajagopal [15]; and (3) Mixture-Coupling theory approach, which combines the advantages of both former approaches, provides a smooth link between geophysics and geochemistry [3, 20-23]. Mixture coupling theory was formally known as Modified Mixture Theory and first proposed by [23] for saturated rocks. It was later extended to unsaturated conditions and non-isothermal conditions [20, 24-26]. As the name Modified Mixture Theory does not fully describe the core of this approach, and also does not make clear distinctions from other “Modified Mixture Theory” such as [27], it is necessary to rename it as Mixture Coupling Theory [3], in this case, the coupling of both fluids and solids as multiphases is specifically addressed (with consideration of secondary phases arising from chemical reaction between groundwater and soils or rock in the future).

The comparison between these three approaches has been summarized by [25]. The mechanics approach has the advantage of being able to deal with a hydro-mechanical coupled model. If chemical reactions are included, this approach has to use formulations from chemistry to interpret chemical transport, due to the knowledge gap between geochemistry and geophysics [28]. Mixture theory has difficulties in obtaining information on the interactions between solid/fluid phases, and also to deal with the coupling of chemicals [12, 13]. Mixture Coupling Theory has successfully overcome the challenges that the above domain approaches face, and has generated more advanced constitutive coupled equations for multiphase flow in deformable porous media [3, 25, 29].

Couplings have been further classified into two groups by Chen and Hicks (2013); external (or structure coupling) and internal coupling. External coupling is a macro-level coupling, whereas, internal coupling may be viewed as micro-level coupling (e.g. chemical transport coupled with groundwater). Mixture Coupling Theory has great potential to deal with internal coupling. It links the force analysis for external coupling and the energy analysis for internal coupling, by using continuum thermomechanics and non-equilibrium thermodynamics [22, 23, 30].

In this paper, Mixture Coupling Theory has been extended to dual chemicals coupling. In particular, Darcy’s Law, Fick’s Law and Biot’s equation have been modified by including chemical potential and sorption, and a new fully-coupled formulation derived.

2 FUNCTION OF BALANCE LAWS FOR AN OPEN SYSTEM

An arbitrary sub-region Ω is chosen in the rock or soil and Γ is the boundary which is assumed to be attached to the solid phase to ensure no solid moves across the boundary. To simplify the discussion, two assumptions are made: (1) there are only two solutes, one is a non-sorbing chemical and the other could be absorbed during transport. The chemical potential of the solutes and water are ξ_{c_s} and ξ_{c_N} and ξ_w, respectively; (2) the continuous gas in the unsaturated zone is at atmospheric pressure, and P_{atm} equals zero. [31, 32].

2.1 Flux definition

The flux is given as :

$$\mathbf{I}_\beta = \tilde{\rho}_\beta(\mathbf{v}_\beta - \mathbf{v}_s); \quad \beta = \text{w or c} \tag{1}$$

in which

- $\mathbf{I}_\beta$ is the flux and $\mathbf{v}_\beta$ is the velocity, respectively.
- $\tilde{\rho}_\beta$ is the fluid density of the water (β=w) or chemical (β=c) component, relative to the unit volume of the fluid-solid mixture. If chemicals are divided into non-adsorbed (c_N) and adsorbed fractions (c_S), then equation (1) may be interpreted as :

$$\mathbf{I}_w = \tilde{\rho}_w(\mathbf{v}_w - \mathbf{v}_s);\ \mathbf{I}_{c_N} = \tilde{\rho}_{c_N}(\mathbf{v}_{c_N} - \mathbf{v}_s)\ ;\ \mathbf{I}_{c_S} = \tilde{\rho}_{c_S}(\mathbf{v}_{c_S} - \mathbf{v}_s) \tag{2}$$

where $\tilde{\rho}_c = \tilde{\rho}_{c_S} + \tilde{\rho}_{c_N}$.

Specifically, the relationship between fluid mass density $\tilde{\rho}_\beta$ and the true mass density ρ_β can be described as

$$\tilde{\rho}_\beta = \phi_\beta \rho_\beta \tag{3}$$

where ϕ_β is the volume fraction of the relevant fluid component.

If S_w is the saturation of the fluid, the relationship between ϕ_β and the porosity of the medium ϕ is given by :

$$\sum \phi_\beta = S_w \phi \tag{4}$$

Equation (4) is based on the assumption that gas transport is ignored here.

2.2 Mass and energy balance

(1) Solid balance equation: In a continuous porous medium, as there is no solid mass flux into the region Ω (note here, it is assumed that sorption will not change the solid mass of the region), the balance equation for the solid can be described as :

$$\frac{\mathrm{D}}{\mathrm{Dt}}\left(\int_\Omega \rho_s \mathrm{d}\Omega\right) = 0 \tag{5}$$

where the solid density is denoted by ρ_s. The material time derivative is given by ;

$$\frac{\mathrm{D}}{\mathrm{Dt}} = \frac{\partial}{\partial t} + \mathbf{v}_s \cdot \nabla \tag{6}$$

(2) Fluid balance equation: Because Ω is an open system, which leads to the exchange of fluid mass (water and non-adsorbed chemical), the balance equation for the fluid (water and chemical, no reaction assumption) can be expressed as

$$\frac{\mathrm{D}}{\mathrm{Dt}}\left(\int_\Omega \rho_\beta \phi_\beta \mathrm{d}\Omega\right) = -\int_\Gamma \mathbf{I}_\beta \cdot \mathbf{n} \mathrm{d}\Gamma \tag{7}$$

However, if the ith chemical may be created or destroyed (reaction term or source term) with the rate Q_β, measured in mass per unit volume of porous medium per unit time, equation (7) can be rewritten as [33] :

$$\frac{\mathrm{D}}{\mathrm{Dt}}\left(\int_\Omega \rho_\beta \phi_\beta \mathrm{d}\Omega\right) = -\int_\Gamma \mathbf{I}_\beta \cdot \mathbf{n} \mathrm{d}\Gamma + \int_\Omega Q_\beta \mathrm{d}\Omega \tag{8}$$

where Q_β is the adsorbed chemical density. Q_β depends on x,y,z and t through its dependence on $\tilde{\rho}_\beta$; it can measure an adsorption rate, a decay rate, a rate of consumption in a chemical reaction, or even a growth or death rate if the tracer is biological.

(3) Helmholtz free energy balance equation:

$$\frac{\mathrm{D}}{\mathrm{Dt}}\left(\int_\Omega \psi \mathrm{d}\Omega\right) = -\int_\Gamma \boldsymbol{\sigma}\mathbf{n}\cdot\mathbf{v}_\mathrm{s}\mathrm{d}\Gamma - \int_\Gamma (\xi_\mathrm{w}\mathbf{I}_\mathrm{w} + \xi_{\mathrm{c_N}}\mathbf{I}_{\mathrm{c_N}} + \xi_{\mathrm{c_S}}\mathbf{I}_{\mathrm{c_S}})\cdot\mathbf{n}\mathrm{d}\Gamma - \mathrm{T}\int_\Omega \gamma \mathrm{d}\Omega \qquad (9)$$

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

2.3 Transport theorem for local zone

Reynold's transport theorem is adopted to give the local balance equations.

The balance equation for the solid mass is :

$$\dot{\rho}_\mathrm{s} + \rho_\mathrm{s}\nabla\cdot\mathbf{v}_\mathrm{s} = 0 \qquad (10)$$

The balance equation for a fluid component is ;

$$\frac{\partial\tilde{\rho}_\beta}{\partial \mathrm{t}} + \tilde{\rho}_\beta\nabla\cdot\mathbf{v}_\mathrm{s} + \nabla\cdot\mathbf{I}_\beta + \mathrm{Q}_\beta = 0 \qquad (11)$$

Note that it is assumed that Q_w and Q_{CN} are zero, as there no loss of water and non-adsorbed chemical during the transport process.

The balance equation for the free energy is :

$$\dot{\psi} + \psi\nabla\cdot\mathbf{v}_\mathrm{s} - \nabla\cdot(\boldsymbol{\sigma}\mathbf{v}_\mathrm{s}) + \nabla\cdot(\xi_\mathrm{w}\mathbf{I}_\mathrm{w} + \xi_{\mathrm{c_N}}\mathbf{I}_{\mathrm{c_N}} + \xi_{\mathrm{c_S}}\mathbf{I}_{\mathrm{c_S}}) = -\mathrm{T}\gamma \le 0 \qquad (12)$$

3 SORPTION AND DISSIPATION ENTROPY

Previous studies for Mixture Coupling Theory have assumed that only one dissipation mechanism exists when fluid moves through the porous media [20, 25, 34]. However, the entropy of this system may also change as chemical mass may be stabilized on the surface of the porous media from the fluid condition in the process of sorption. The reasons for entropy change, including the sorption, may be summarized as: (1) friction generated at the solid/water boundary; (2) two processes operate for the chemicals in the fluid: the dissipation between the chemical fluids/solid boundary, which is covered in process (1), and partitioning of the chemicals during the sorption process. Non-equilibrium thermodynamics has been used to derive the dissipation and sorption function [34], which is :

$$0 \le \mathrm{T}\gamma = -\mathbf{I}_{\mathrm{w}} \cdot \nabla \xi_{\mathrm{w}} - \mathbf{I}_{\mathrm{c_N}} \cdot \nabla \xi_{\mathrm{c_N}} - \mathbf{I}_{\mathrm{c_S}} \cdot \nabla \xi_{\mathrm{c_S}} - \mathrm{Q} \cdot \Delta \xi_{\mathrm{q}} \tag{13}$$

where Q can be positive or negative, representing dissolution, sorption or chemical reaction of a substance. $\Delta \xi_{\mathrm{q}}$ represents the change of chemical potential after reducing/increasing freedom of molecules.

To focus on the coupling of the two chemicals, and simplify the discussion, the term $\mathrm{Q}_{\mathrm{c_S}} \cdot \Delta \xi_{\mathrm{c_S}}$, which shows the sorption process, could influence the diffusion process, and has been ignored in the analysis. Thus, equation (13) can then be rewritten as :

$$0 \le \mathrm{T}\gamma = -\mathbf{I}_{\mathrm{w}} \cdot \nabla \xi_{\mathrm{w}} - \mathbf{I}_{\mathrm{c_N}} \cdot \nabla \xi_{\mathrm{c_N}} - \mathbf{I}_{\mathrm{c_S}} \cdot \nabla \xi_{\mathrm{c_S}} \tag{14}$$

Equation (14) has presented the relationship between flux and chemical potential.

The total fluid mass density, $\tilde{\rho}_{\mathrm{f}}$, can be defined as :

$$\tilde{\rho}_{\mathrm{f}} = \tilde{\rho}_{\mathrm{w}} + \tilde{\rho}_{\mathrm{c_N}} + \tilde{\rho}_{\mathrm{c_S}} \tag{15}$$

The fluid barycentric velocity, which is a velocity of one body relative to the center of mass of a system, is defined as the mass flux divided by the mass density, as in :

$$\mathbf{v}_{\mathrm{f}} = \frac{\tilde{\rho}_{\mathrm{w}} \mathbf{v}_{\mathrm{w}}}{\tilde{\rho}_{\mathrm{f}}} + \frac{\tilde{\rho}_{\mathrm{c_N}} \mathbf{v}_{\mathrm{c_N}}}{\tilde{\rho}_{\mathrm{f}}} + \frac{\tilde{\rho}_{\mathrm{c_S}} \mathbf{v}_{\mathrm{c_S}}}{\tilde{\rho}_{\mathrm{f}}} \tag{16}$$

Since the diffusion fluxes of the water and chemical relative to the barycentric motion can be written as :

$$\mathbf{J}_{\beta} = \rho\%_{\beta}(\mathbf{v}_{\beta} - \mathbf{v}_{\mathrm{f}}) \tag{17}$$

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

$$\mathbf{J}_{\beta} = \mathbf{I}_{\beta} - \rho\%_{\beta}(\mathbf{v}_{\mathrm{f}} - \mathbf{v}_{\mathrm{s}}) \tag{18}$$

As the Darcy velocity can also be described through the equation :

$$\mathbf{u}_{\mathrm{D}} = \mathrm{S}_{\mathrm{w}}\phi(\mathbf{v}_{\mathrm{f}} - \mathbf{v}_{\mathrm{s}}) \tag{19}$$

the entropy production of the fluid (equation (14)) can be rearranged as :

$$0 \le \mathrm{T}\gamma = -\mathbf{u}_{\mathrm{D}} \cdot \nabla \mathrm{p} - (\mathbf{J}_{\mathrm{w}} \cdot \nabla \xi_{\mathrm{w}} + \mathbf{J}_{\mathrm{c_N}} \cdot \nabla \xi_{\mathrm{c_N}} + \mathbf{J}_{\mathrm{c_S}} \cdot \nabla \xi_{\mathrm{c_S}}) \tag{20}$$

Using the Gibbs-Duhem equation for the fluid leads to :

$$\rho_{\mathrm{w}} \nabla \xi_{\mathrm{w}} + \rho_{\mathrm{c_N}} \nabla \xi_{\mathrm{c_N}} + \rho_{\mathrm{c_S}} \nabla \xi_{\mathrm{c_S}} = \nabla \mathrm{p_p} \tag{21}$$

where $\mathrm{p_p}$ is the pore fluid pressure of the fluid mixture (i.e. the water and chemical combined) [35].

As there are only two independent diffusion fluxes within the three fluxes system:

$$\mathbf{J}_{\mathrm{w}} + \mathbf{J}_{\mathrm{c_N}} + \mathbf{J}_{\mathrm{c_S}} = 0 \tag{22}$$

the entropy production equation (20) can be further rearranged

$$0 \le \mathrm{T}\gamma = -\mathbf{u}_{\mathrm{D}} \cdot \nabla \mathrm{p_p} - \mathbf{J}_{\mathrm{c_N}} \cdot \nabla(\xi_{\mathrm{c_N}} - \xi_{\mathrm{w}}) - \mathbf{J}_{\mathrm{c_S}} \cdot \nabla(\xi_{\mathrm{c_S}} - \xi_{\mathrm{w}}) \tag{23}$$

in which :

$-\mathbf{u}_{\mathrm{D}} \cdot \nabla \mathrm{p_p}$ shows the water flow driven by internal water potential difference;

$\mathbf{J}_{\mathrm{c_N}} \cdot \nabla(\xi_{\mathrm{c_N}} - \xi_{\mathrm{w}})$ describes non-sorption chemical diffusion into water, and

$\mathbf{J}_{\mathrm{c_S}} \cdot \nabla(\xi_{\mathrm{c_S}} - \xi_{\mathrm{w}})$ represents sorption-chemical diffusion into water.

4 COUPLED DIFFUSION LAW AND DARCY'S LAW

Equation (23) explains the entropy contribution of flow and relative driving force. Each driving force of a specific flux may also have a coupling influence on other fluxes, which leads to the discussion of interactions between flow and driving force by using "Phenomenological equations". Such equations expressed the linear dependence of the three flows on their corresponding forces. The coupling between the three flows, $\rho_{\mathrm{f}}\mathbf{u}_{\mathrm{D}}$, $\mathbf{J}_{\mathrm{c_N}}$ and $\mathbf{J}_{\mathrm{c_S}}$, and the major three driving forces, $\nabla \mathrm{p}_{\mathrm{p}}$ and $\nabla(\xi_{\mathrm{c_N}} - \xi_{\mathrm{w}})$, $\nabla(\xi_{\mathrm{c_S}} - \xi_{\mathrm{w}})$, can be obtained from :

$$\rho_{\mathrm{f}}\mathbf{u}_{\mathrm{D}} = -\left(\frac{\mathrm{L}_{11}}{\rho_{\mathrm{f}}}\right)\nabla \mathrm{p}_{\mathrm{p}} - \mathrm{L}_{12}\nabla(\xi_{\mathrm{c_N}} - \xi_{\mathrm{w}}) - \mathrm{L}_{13}\nabla(\xi_{\mathrm{c_S}} - \xi_{\mathrm{w}}) \tag{24}$$

$$\mathbf{J}_{\mathrm{c_N}} = -\left(\frac{\mathrm{L}_{21}}{\rho_{\mathrm{f}}}\right)\nabla \mathrm{p}_{\mathrm{p}} - \mathrm{L}_{22}\nabla(\xi_{\mathrm{c_N}} - \xi_{\mathrm{w}}) - \mathrm{L}_{23}\nabla(\xi_{\mathrm{c_S}} - \xi_{\mathrm{w}}) \tag{25}$$

$$\mathbf{J}_{\mathrm{c_S}} = -\left(\frac{\mathrm{L}_{31}}{\rho_{\mathrm{f}}}\right)\nabla \mathrm{p}_{\mathrm{p}} - \mathrm{L}_{32}\nabla(\xi_{\mathrm{c_N}} - \xi_{\mathrm{w}}) - \mathrm{L}_{33}\nabla(\xi_{\mathrm{c_S}} - \xi_{\mathrm{w}}) \tag{26}$$

in which L_{ij} denotes a set of phenomenological coefficients. Here, mass transport is assumed to be through an isotropic medium.

The discussion of Phenomenological equations and Onsager Coefficients is explained in recent studies [36].

Equations (24), (25) and (26) describe the coupled diffusion fluxes and water flow with coupled influence of water pressure and chemical potential difference. However, chemical concentration is easier to measure in practice than chemical potential. The following discussion will establish the relationship between chemical potential with chemical concentration.

The Gibbs-Duhem equation describes the link between the change of chemical potential with temperature and pressure. In this paper, it is assumed that an isothermal and constant pressure condition exists for the mixture at the local region scale. Thus, the relationship between chemical potential and mass fraction is derived as:

$$C_{c_S}(d\xi_{c_S})_p + C_{c_N}(d\xi_{c_N})_p + C_w(d\xi_w)_p = 0 \tag{27}$$

in which C_c and C_w are the solute and diluent mass fractions, respectively, which can be further defined as

$$C_w = \frac{\rho_w}{\rho_f} = \frac{\tilde{\rho}_w}{\tilde{\rho}_f};\quad C_{c_N} = \frac{\rho_{c_N}}{\rho_f} = \frac{\tilde{\rho}_{c_N}}{\tilde{\rho}_f};\quad C_c = \frac{\rho_{c_S}}{\rho_f} = \frac{\tilde{\rho}_{c_S}}{\tilde{\rho}_f} \tag{28}$$

Also, chemical potential can be interpreted by using standard non-equilibrium thermodynamics as

$$\nabla(\xi_{c_S} - \xi_w) = (v_{c_S} - v_w)\nabla p_p + \frac{1}{C_w}\frac{\partial \xi_{c_S}}{\partial C_{c_S}}\nabla C_{c_S} \tag{29}$$

$$\nabla(\xi_{c_N} - \xi_w) = (v_{c_N} - v_w)\nabla p_p + \frac{1}{C_w}\frac{\partial \xi_{c_N}}{\partial C_{c_N}}\nabla C_{c_N} \tag{30}$$

in which $v_{c_N} = \frac{\partial}{\partial C_{c_N}}\left(\frac{1}{\rho_{c_N}}\right)$, $v_{c_S} = \frac{\partial}{\partial C_{c_S}}\left(\frac{1}{\rho_{c_S}}\right)$ and $v_w = \frac{\partial}{\partial C_w}\left(\frac{1}{\rho_w}\right)$ presents the partial specific volumes of the solute (non-sorption and sorption) and diluent, respectively. These quantities should follow the thermodynamic identities,

$$v_{c_N} = \frac{\partial \xi_{c_N}}{\partial p},\; v_{c_S} = \frac{\partial \xi_{c_S}}{\partial p},\; v_w = \frac{\partial \xi_w}{\partial p} \tag{31}$$

Additionally, equations (24) and (25) can be rewritten if $\rho_f(v_{fc} - v_{fw}) << 1$, as

$$\mathbf{u}_D = -\frac{\mathbf{K}k_{rw}}{\mu}\left(\nabla p_p - r_{c_N}\frac{\rho_f}{C_w}\frac{\partial \xi_{c_N}}{\partial C_{c_N}}\nabla C_{c_N} - r_{c_S}\frac{\rho_f}{C_w}\frac{\partial \xi_{c_S}}{\partial C_{c_S}}\nabla C_{c_S}\right) \tag{32}$$

$$\mathbf{J}_{c_N} = \frac{L_{c_N}\rho_f}{p_p}\nabla p_p - \rho_f \mathbf{D}_{c_N}\cdot\nabla C_{c_N} - \rho_f \mathbf{D}_{c_{N\text{-}S}}\cdot\nabla C_{c_S} \tag{33}$$

$$\mathbf{J}_{c_S} = \frac{L\rho_f}{p_p}\nabla p_p - \rho_f \mathbf{D}_{c_{S\text{-}N}}\cdot\nabla C_{c_N} - \rho_f \mathbf{D}_{c_S}\cdot\nabla C_{c_S} \tag{34}$$

in which

$$\frac{\mathbf{K}k_{\mathrm{rw}}}{\mu_{\mathrm{w}}}=\frac{\mathrm{L}_{11}}{\left(\rho_{\mathrm{f}}\right)^{2}};\ \mathrm{r}_{\mathrm{c_N}}=-\frac{\mathrm{L}_{21}}{\mathrm{L}_{11}};\ \mathrm{r}_{\mathrm{c_S}}=-\frac{\mathrm{L}_{31}}{\mathrm{L}_{11}};\mathrm{L}_{\mathrm{c_N}}=\frac{\mathrm{L}_{21}\mathrm{p}_{\mathrm{p}}}{\left(\rho_{\mathrm{f}}\right)^{2}};\ \mathrm{L}_{\mathrm{c_S}}=\frac{\mathrm{L}_{31}\mathrm{p}_{\mathrm{p}}}{\left(\rho_{\mathrm{f}}\right)^{2}};$$

$$\mathrm{D}_{\mathrm{c_N}}=\frac{\mathrm{L}_{22}}{\mathrm{C}_{\mathrm{w}}\left(\rho_{\mathrm{f}}\right)^{2}}\frac{\partial\xi_{\mathrm{c_N}}}{\partial\mathrm{C}_{\mathrm{c_N}}};\mathrm{D}_{\mathrm{c_S}}=\frac{\mathrm{L}_{33}}{\mathrm{C}_{\mathrm{w}}\left(\rho_{\mathrm{f}}\right)^{2}}\frac{\partial\xi_{\mathrm{c_S}}}{\partial\mathrm{C}_{\mathrm{c_S}}};\ \mathrm{D}_{\mathrm{c_{S\text{-}N}}}=\frac{\mathrm{L}_{23}}{\mathrm{C}_{\mathrm{w}}\left(\rho_{\mathrm{f}}\right)^{2}}\frac{\partial\xi_{\mathrm{c_S}}}{\partial\mathrm{C}_{\mathrm{c_S}}};\ \mathrm{D}_{\mathrm{c_{N\text{-}S}}}=\frac{\mathrm{L}_{32}}{\mathrm{C}_{\mathrm{w}}\left(\rho_{\mathrm{f}}\right)^{2}}\frac{\partial\xi_{\mathrm{c_S}}}{\partial\mathrm{C}_{\mathrm{c_S}}};\quad(35)$$

and μ_{w} is the water's dynamic viscosity.

In equation (35), L_{11} links to the typical Darcian model, L_{22} to the Fickian model, $\frac{\mathrm{L}_{21}}{\mathrm{L}_{11}}$ to the reflection coefficient which shows the coupled influence of chemical concentration on water flow, and $\mathrm{L}=\frac{\mathrm{L}_{21}\mathrm{p}_{\mathrm{p}}}{\left(\rho_{\mathrm{f}}\right)^{2}}$ represents the fluid pressure influence on chemical diffusion, which may exist in conditions of very high fluid pressure gradients, or in gas transport.

From the above analysis of equations (32), (33) and (35), Darcy's Law and Fick's Law have been modified from a thermodynamic point of view, with the coupled influence between groundwater flow and chemical diffusion. The modification of the Darcy velocity includes the effect of the chemical concentration in Eq. (27). By studying this model, one will realize that the effect of the chemical concentration is actually to reduce or increase the Darcian contribution. The change of the Darcian contribution also has a consequent influence on mechanical preformation, which will be discussed later. The modification of the Fickian model includes the effect of dual chemical coupling and water pressure. By extension of this model, one will realize that chemical diffusion can be changed by other chemical diffusion processes, and increasing water pressure acts to reduce the diffusion process.

Onsager's symmetry theorem [37], which is a rigorous description of thermal influences on the electrical current and vice versa, is not used here, as it is based on an assumption of a balanced energy flow between a few subsystems by neglecting the loss during heat conduction and energy conversion and relation. It is validated in an ideal system only with an equilibrium condition. However, soils and rock systems create a strongly irreversible and non-equilibrium process, in which Onsager's symmetry may not be applicable.

5 STRESS AND STRAIN RESPONSE

5.1 Helmholtz free energy of the system

After discussion of coupled fluxes in section 4, attention is now given to link physical deformation of porous media with the fluxes inside. By assuming that the rock maintains mechanical equilibrium ($\nabla\cdot\boldsymbol{\sigma}=0$) and using equations (12) and (13), ψ can be derived as

$$\dot{\psi}+\psi\nabla\cdot\mathbf{v}_{\mathrm{s}}-\left(\boldsymbol{\sigma}:\nabla\mathbf{v}_{\mathrm{s}}\right)+\xi_{\mathrm{w}}\nabla\cdot\mathbf{I}_{\mathrm{w}}+\xi_{\mathrm{c_S}}\nabla\cdot\mathbf{I}_{\mathrm{c_S}}+\xi_{\mathrm{c_N}}\nabla\cdot\mathbf{I}_{\mathrm{c_N}}=0 \qquad (36)$$

Continuum mechanics has defined the state of the porous media deformation, which will be used in this paper [38] as follows:

$$\mathbf{F}=\frac{\partial\mathbf{x}}{\partial\mathbf{X}}(\mathbf{X},\mathrm{t}),\ \mathbf{E}=\frac{1}{2}(\mathbf{F}^{\mathbf{T}}\mathbf{F}-\mathbf{I}),\ \mathrm{J}=\frac{\mathrm{d}\Omega}{\Omega_0},\ \dot{\mathrm{J}}=\mathrm{J}\nabla\cdot\mathbf{v}_{\mathrm{s}},\ \mathbf{T}=\mathrm{J}\mathbf{F}^{-1}\boldsymbol{\sigma}\mathbf{F}^{\mathbf{-T}} \qquad (37)$$

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

By using equations (36) and (37), the free energy in the reference configuration, Ψ , can be derived as

$$\dot{\Psi}=\mathrm{tr}\left[\mathbf{T}\dot{\mathbf{E}}\right]+\xi_{\mathrm{w}}\dot{\mathrm{m}}_{\mathrm{w}}+\xi_{\mathrm{c_N}}\dot{\mathrm{m}}_{\mathrm{c_N}}+\xi_{\mathrm{c_S}}\dot{\mathrm{m}}_{\mathrm{c_S}}, \qquad (38)$$

where

$$\Psi=\mathrm{J}\psi;\quad \mathrm{m}_\beta=\mathrm{J}\tilde{\rho}_\beta=\mathrm{J}\phi_\beta\rho_\beta. \qquad (39)$$

in which m_β is the mass density of the fluid in the reference configuration.

5.2 Pore fluid

Fluids may exist both in the pore spaces as the bulk phase, or in clay platelets as molecular-scale entities [3] and surface of the solids (for sorption). Thermodynamic relationships can not be used for molecular scale forces, but can be used for the bulk fluids in the pore spaces. Hence ψ_{pore} (the Helmholtz free energy density of the pore fluid) can be obtained as

$$\psi_{\mathrm{pore}} = -\mathrm{p}_{\mathrm{p}} + \xi_{\mathrm{c_N}}\rho_{\mathrm{c_N}} + \xi_{\mathrm{c_S}}\rho_{\mathrm{c_S}} + \xi_{\mathrm{w}}\rho_{\mathrm{w}} \tag{40}$$

in which p_{p} is the pore fluid pressure. From the Gibbs-Duhem equation, the relationship between pressure change and chemical concentration can be obtained by

$$\dot{\mathrm{p}}_{\mathrm{p}} = \dot{\xi}_{\mathrm{c_N}}\rho_{\mathrm{c_N}} + \dot{\xi}_{\mathrm{w}}\rho_{\mathrm{w}} + \dot{\xi}_{\mathrm{c_S}}\rho_{\mathrm{c_S}} \tag{41}$$

Equation (40) may be further rearranged by as

$$\dot{\psi}_{\mathrm{pore}} = -\dot{\mathrm{p}}_{\mathrm{p}} + \dot{\xi}_{\mathrm{c_N}}\rho_{\mathrm{c_N}} + \dot{\xi}_{\mathrm{c_S}}\rho_{\mathrm{c_S}} + \dot{\xi}_{\mathrm{w}}\rho_{\mathrm{w}} + \xi_{\mathrm{c_N}}\dot{\rho}_{\mathrm{c_N}} + \xi_{\mathrm{c_S}}\dot{\rho}_{\mathrm{c_S}} + \dot{\xi}_{\mathrm{w}}\dot{\rho}_{\mathrm{w}} \tag{42}$$

Thus by substituting equation (41) into equation (42), this leads to

$$\dot{\psi}_{\mathrm{pore}} = \xi_{\mathrm{c_N}}\dot{\rho}_{\mathrm{c_N}} + \xi_{\mathrm{c_S}}\dot{\rho}_{\mathrm{c_S}} + \xi_{\mathrm{w}}\dot{\rho}_{\mathrm{w}} \tag{43}$$

5.3 "Wet" matrix

The free energy of the "wet matrix", including solid and surface molecular entities, can not be directly derived because non-equilibrium thermodynamics is not applicable to potential molecular force. Thus the free energy may be found by subtracting the contribution $\mathrm{J}\,\phi\psi_{\mathrm{pore}}$, due to the pore fluid, from the total free energy Ψ. If $\upsilon = \mathrm{J}\,\phi$ is the pore volume per unit reference volume, the free energy density of the wet matrix may be written as

$$\frac{\partial}{\partial \mathrm{t}}\left(\Psi - \mathrm{J}\,\phi\psi_{\mathrm{pore}}\right) = \mathrm{tr}[\mathbf{T}\dot{\mathbf{E}}] + \mathrm{p}_{\mathrm{p}}\dot{\upsilon} + \xi_{\mathrm{c_S}}\dot{\mathrm{m}}_{\mathrm{c_S}} + \xi_{\mathrm{c_S}}\dot{\mathrm{m}}_{\mathrm{c_N}} + \xi_{\mathrm{w}}\dot{\mathrm{m}}_{\mathrm{w}} \tag{44}$$

To simply the discussion, $\xi_{\mathrm{c_S}}\dot{\mathrm{m}}_{\mathrm{c_S}} + \xi_{\mathrm{c_S}}\dot{\mathrm{m}}_{\mathrm{c_N}} + \xi_{\mathrm{w}}\dot{\mathrm{m}}_{\mathrm{w}}$ is assumed to be one fluid and described as bound fluid with chemical potential ξ_{b} and mass density m_{b}.

The dual potential, W, which is employed in the following discussion for reasons of convenience, can be described as

$$W = (\Psi - J\,\phi\psi_{\mathrm{pore}}) - p_p\upsilon - \xi_b m_b \qquad (45)$$

If W is expressed as a function of $\mathbf{E}$, p_p ξ_b, the expressions for $\mathbf{T}$ and υ m_b can be obtained. From the implication of Equation (45), the time derivative of $W(E, p_p, \xi_b)$ satisfies the following relationship:

$$\dot{W}(\mathbf{E}, p, \xi_b) = \mathrm{tr}(\mathbf{T}\dot{\mathbf{E}}) - \dot{p}_p\upsilon - \dot{\xi}_b m_b \qquad (46)$$

so that T_{ij}, υ and m_b can be derived as

$$T_{ij} = \left(\frac{\partial W}{\partial E_{ij}}\right)_{p_p,\xi_b}, \quad \upsilon = -\left(\frac{\partial W}{\partial p_p}\right)_{E_{ij},\xi_b}, \quad m_b = -\left(\frac{\partial W}{\partial \xi_b}\right)_{E_{ij},p_p} \qquad (47)$$

and also equation (46) can be rearranged as

$$\dot{W}(\mathbf{E}, p_p, \xi_b) = \left(\frac{\partial W}{\partial E_{ij}}\right)_{p_p}\dot{E}_{ij} + \left(\frac{\partial W}{\partial p_p}\right)_{E_{ij}}\dot{p}_p + \left(\frac{\partial W}{\partial \xi_b}\right)_{E_{ij}}\dot{\xi}_b \qquad (48)$$

By differentiating equations (47) with respect to time, the evolution of stress, pore volume fraction and bound fluid can be given as

$$\dot{T}_{ij} = L_{ijkl}\dot{E}_{kl} - M_{ij}\dot{p}_p + S_{ij}\dot{\xi}_b \qquad (49)$$

$$\dot{\upsilon} = M_{ij}\dot{E}_{ij} + Q\dot{p}_p + B\dot{\xi}_b \qquad (50)$$

$$\dot{m}_b = S_{ij}\dot{E}_{ij} + B\dot{p}_p + Z\dot{\xi}_b \qquad (51)$$

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

$$L_{ijkl} = \left(\frac{\partial T_{ij}}{\partial E_{kl}}\right)_{p_p,\xi_b} = \left(\frac{\partial T_{kl}}{\partial E_{ij}}\right)_{p_p,\xi_b}$$

$$M_{ij} = -\left(\frac{\partial T_{ij}}{\partial p_p}\right)_{E_{ij},\xi_b} = \left(\frac{\partial \upsilon}{\partial E_{ij}}\right)_{p_p,\xi_b}$$

$$Q = \left(\frac{\partial \upsilon}{\partial p_p} \right)_{E_{ij}, \xi_b} \tag{52}$$

$$S_{ij} = \left(\frac{\partial T_{ij}}{\partial \xi_b} \right)_{p_p, E_{ij}} = \left(\frac{\partial m_b}{\partial E_{ij}} \right)_{p_p, \xi_b}$$

$$B = \left(\frac{\partial \upsilon}{\partial \xi_b} \right)_{E_{ij}, p_p} = \left(\frac{\partial m_b}{\partial p_p} \right)_{E_{ij}, p_p}$$

$$Z = \left(\frac{\partial m_b}{\partial \xi_b} \right)_{E_{ij}, p_p}$$

6 THE INFLUENCE OF CHEMICAL POTENTIAL ON TRANSPORT

6.1 Chemical potential

Three chemical components are present in this paper including solute (conservative transport of chemical, and chemical with sorption function) and diluent (water). Using Eq (41) results in

$$\dot{p}_p = \rho_w \dot{\xi}_w + \rho_{c_N} \dot{\xi}_{c_N} + \rho_{c_S} \dot{\xi}_{c_S} \tag{53}$$

and then

$$\dot{\xi}_w = \left(\frac{1}{\rho_w} \right) \left(\dot{p}_p - \rho_{c_N} \dot{\xi}_{c_N} - \rho_{c_S} \dot{\xi}_{c_S} \right) \tag{54}$$

The solute chemical potential may be described as [34] :

$$\xi_c = g_c(p, T) + \left(\frac{RT}{M_c} \right) \ln a_c \tag{55}$$

where

- g_c is assumed to be ignored because of the week dependence of ξ_c on g_c.
- M_c is the molar mass and R is the universal gas constant
- a_c is the activity of the solute.

The relationship between a_c and x_c (the mole fraction) can be described as

$$a_c = r_c x_c \tag{56}$$

where r_c is the activity coefficient. For an ideal solution, equation (56) leads to

$$a_c = x_c \tag{57}$$

Thus, the chain relationship between x_c and the solute mass fraction C_c is given through

$$C_c = \frac{x_c M_c}{x_c M_c + (1 - x_c) M_w} \tag{58}$$

6.2 Reactive and non-reactive chemical transport

The general chemical transport equation can be derived by using the mass density equation (3) and the partial mass equation (11), and substituting equation (18) and employing the Euler identity:

$$\frac{\partial}{\partial t}(S_w \phi \rho_\beta) + J \nabla \cdot (\rho_\beta \mathbf{u}_D) + J \nabla \cdot \mathbf{J}_\beta - Q_\beta = 0 \tag{59}$$

By assuming the fluid is incompressible and introducing the mass fraction $C_\beta = \frac{\rho_\beta}{\rho_f}$, equation (59) can be further rearranged as

$$\frac{\partial}{\partial t}(S_w \phi \rho_f C_\beta) + \nabla \cdot (\rho_f C_\beta \mathbf{u}_D) + \nabla \cdot \mathbf{J}_\beta - Q_\beta = 0 \tag{60}$$

As the fluid fraction and diffusion flux follows the restriction of $\sum_\beta C_\beta = 1$ and $\sum_\beta \mathbf{J}_\beta = 0$, respectively, by summation of all the fluid components, equation (60) can be derived as :

$$\frac{\partial}{\partial t}(\upsilon S_w \rho_f) + \nabla \cdot (\rho_f \mathbf{u}_D) - Q_\beta = 0 \tag{61}$$

By invoking equation (61), equation (60) can be derived as

$$S_w \upsilon \rho_f \frac{\partial C_\beta}{\partial t} + \rho_f \mathbf{u}_D \cdot \nabla C_\beta + \nabla \cdot \mathbf{J}_\beta - Q_\beta = 0 \qquad (62)$$

7 GOVERNING FIELD EQUATIONS

The average pore pressure $\bar{p}$ is used in the paper. In the condition of mechanical equilibrium, $\bar{p}$ is assumed to equal the pore pressure p_p. The relationship between p_p, $\bar{p}$, p_w and p_g is given by

$$\bar{p} = p_p = S_w p_w + S_g p_g \approx S_w p_w \qquad (63)$$

The time derivation of equation (63) is

$$\dot{\bar{p}} = S_w \frac{\partial p_w}{\partial t} + \frac{\theta}{\phi} p_w \frac{\partial p_w}{\partial t} \qquad (64)$$

Lewis and Scherefler (1987) has discussed equation (64), and θ is the specific moisture content (related to pressure). Note that the potential chemical effects on specific moisture have been ignored here to simplify the discussion.

7.1 Solid matrix deformation

The general constitutive equations (49) and (50) describes the changes in solid stress and volume fraction in the coupling with pore pressure, chemical concentration and strain. These two equations can be further simplified by using the following assumptions.

- Small strain assumption: Green Strain tensor E_{ij} and the Piola-Kirchhoff stress T_{ij} can be replaced by strain tensor ε_{ij} and Cauchy stress σ_{ij}, that is :

$$E_{ij} = \varepsilon_{ij}, \ T_{ij} = \sigma_{ij} \qquad (65)$$

where $\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$, in which u_i $(i = 1, 2, 3)$ is the displacement component.

Under the mechanical equilibrium condition, the following relationship can be obtained to simplify the discussion

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0 \tag{66}$$

- Physical and geometrical linearization: The parameters L_{ijkl}, M_{ij}, Q are assumed to be material-dependent constants, so that the non-linearity is then of a geometrical nature and associated with large deformations.
- Material isotropy: for isotropic materials the tensor M_{ij} is diagonal, so that it can be written in the form of the scalar α, called the Biot coefficient :

$$M_{ij} = \alpha \delta_{ij} \tag{67}$$

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

$$L_{ijkl} = G(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \left(K - \frac{2G}{3}\right)\delta_{ij}\delta_{kl} \tag{68}$$

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

From the above simplification, the respective equations for the solid matrix and pore volume fraction can be derived as

$$\dot{\sigma}_{ij} = \left(K - \frac{2G}{3}\right)\dot{\varepsilon}_{kk}\delta_{ij} + 2G\dot{\varepsilon}_{ij} - \alpha\dot{\bar{p}}\delta_{ij} \tag{69}$$

$$\dot{\upsilon} = \alpha\dot{\varepsilon}_{ii} + Q\dot{\bar{p}} \tag{70}$$

where, in a poro-elastic manner, α has a relationship with the bulk moduli, K and K_s, as:

$$\alpha = 1 - \frac{K}{K_s} \tag{71}$$

in which K_s is the bulk modulus of the solid matrix. The void compressibility, Q, can be described as

$$Q = \frac{\alpha - \phi}{K_s} \tag{72}$$

Note that the swelling term $\dot{m}_b$, which describes the mass density change in the “wet” matrix, has been ignored to simplify the discussion and focus on the dual chemical osmosis.

Thus, equation (49) can be rearranged as

$$G\nabla^2 \dot{\mathbf{u}} + \left(\frac{G}{1-2\nu}\right)\nabla(\nabla \cdot \dot{\mathbf{u}}) - \alpha \nabla \dot{\bar{p}} = 0 \tag{73}$$

By substituting the definition of average pressure from (57) into (66), equation (73) can be further developed as :

$$G\nabla^2 \dot{\mathbf{u}} + \left(\frac{G}{1-2\nu}\right)\nabla(\nabla \cdot \dot{\mathbf{u}}) - \alpha \left[\left(S_w + \frac{\theta}{\phi} p_w\right)\right]\nabla \dot{p}_w = 0 \tag{74}$$

7.2 Water transport coupled with deformation and dual chemical osmosis
From equations (61) and (70), and by introducing equation (55) and (58), this leads to

$$\begin{aligned} & S_w \rho_f \zeta \nabla \cdot \dot{\mathbf{u}} + S_w \rho_f Q \dot{\bar{p}} + \phi \rho_f \frac{\partial S_w}{\partial t} + \phi S_w \frac{\partial \rho_f}{\partial t} + \rho_{Tf}\left[-\nabla \cdot \frac{\mathbf{K} k_{rw}}{\mu}\left(\nabla p_w - \right.\right. \\ & \left.\left. \rho_f r_{c_N} \frac{RT}{M_{c_N}} \frac{1}{C_{c_N} C_w} \nabla C_{c_N} - \rho_f r_{c_S} \frac{RT}{M_{c_S}} \frac{1}{C_{c_S} C_w} \nabla C_{c_S}\right)\right] = 0 \end{aligned} \tag{75}$$

Equation (75) shows that the dual chemical osmosis will have a strong influence on the pore water pressure change. It can be further reformed with consideration of the rate of change of saturation and the water density function [39] :

$$\phi \frac{\partial S_w}{\partial t} + \frac{\phi S_w}{\rho_{Tf}} \frac{\partial \rho_f}{\partial t} = \theta \frac{\partial p_w}{\partial t} + \phi \frac{S_w}{K_w} \frac{\partial p_w}{\partial t} = \left(\theta + \phi \frac{S_w}{K_w}\right)\frac{\partial p_w}{\partial t} \tag{76}$$

where K_w is the bulk modulus of water, such that equation (75) can be derived as

$$-\left[\nabla \cdot \frac{\mathbf{K} k_{rw}}{\mu}\left(\nabla p_w - \frac{\rho_{Tf} r_{c_s} RT}{M_{c_s} C_{c_s} C_w} \nabla C_{c_N} - \frac{\rho_{Tf} r_{c_N} RT}{M_{c_N} C_{c_N} C_w} \nabla C_{c_N}\right)\right] + S_w \alpha \nabla \cdot \dot{\mathbf{u}} + S_w \left[Q\left(1 + \frac{\theta}{\phi} p_w\right) + \left(1 + \frac{\phi}{K_w}\right)\right]\frac{\partial p_w}{\partial t} = 0$$

(77)

7.3 Chemical transport with coupled dual chemical osmosis

From equations (32), (33) and (62) the chemical transport equation of a non-sorbing chemical with coupled dual chemical osmosis can be obtained as

$$-L\nabla\left(\frac{1}{p_w}\nabla p_w\right)-D\nabla^2 C_{c_N}+S_w\phi\frac{\partial C_{c_N}}{\partial t}-\left[\frac{\mathbf{K}k_{rw}}{\mu}\left(\nabla p_w-\frac{\rho_{Tf}\,r\,RT}{M_{c_N}C_{c_N}C_w}\nabla C_{c_N}-\frac{\rho_{Tf}\,r_{c_S}RT}{M_{c_S}C_{c_S}C_w}\nabla C_{c_S}\right)\right]\cdot\nabla C_{c_N}=0 \tag{78}$$

And for the sorbing chemicals the equation is given as

$$-L\nabla\left(\frac{1}{p_w}\nabla p_w\right)-D\nabla^2 C_{c_S}+S_w\phi\frac{\partial C_{c_S}}{\partial t}-\left[\frac{\mathbf{K}k_{rw}}{\mu}\left(\nabla p_w-\frac{\rho_{Tf}\,r_{c_S}RT}{M_{c_S}C_{c_S}C_w}\nabla C_{c_S}-\frac{\rho_{Tf}\,r\,RT}{M_{c_N}C_{c_N}C_w}\nabla C_{c_N}\right)\right]\cdot\nabla C_{c_S}-Q=0 \tag{79}$$

where $Q=-\rho(1-\phi)S(t)$ [33], in which S_t is the mass of solute absorbed. By assuming instantaneous kinetics and reaction equilibrium, this leads to

$$S_t = k_d C_{c_s} \tag{80}$$

The term S could also be expressed as linear, Langmuir, Freundlich, Quadratic, Generalized Langmuir and exponential, based on a microscopic sorption mechanics analysis. Further details can be found in [33]. As this paper is focused on the osmosis and entropy function, such details will not be discussed.

7.4 Discussion and summary

The function of dual osmosis has been incorporated within chemical transport equations. This shows that multiple chemicals may have a combined influence on both water and chemical transport. Equation (78) and (79) are new formulations of chemical transport which consider dual chemical osmosis ($-\frac{\rho_{Tf}\,r_{c_S}RT}{M_{c_S}C_{c_S}C_w}\nabla C_{c_S}-\frac{\rho_{Tf}\,r\,RT}{M_{c_N}C_{c_N}C_w}\nabla C_{c_N}$), and also include the influence of pressure ($L\nabla\left(\frac{1}{p_w}\nabla p_w\right)$) on chemical transport. The general chemical transport equation in groundwater [33] is a special case of these two equations, which does not consider the two osmotic couplings. This general equation will lead to an incorrect prediction of chemicals transport in a very low permeability porous media, as osmotic and diffusion processes are the dominant forces driving the movement of water and chemicals

Equation (77) has further extended Darcy's Law by including a dual chemical osmosis term. Without considering this, equation (77) resolves to the same term for single chemical osmosis presented in [25]. Equation (74) shows the influence of pore water pressure on mechanical deformation, which indirectly links the influence of chemical dual osmosis. The equation is the same as in [25]. Equation (74) can also be obtained as approximations with confined boundary conditions from mixture theory that has been rigorously developed [14, 15].

8 Conclusion

In this study the concept and mathematical equation of dual chemical osmosis has been presented. Mixture Coupling theory has been further extended, resulting in a new constitutive unsaturated coupled hydro-mechanical-chemical model for very low permeability porous media. The potential of Mixture Coupling theory to bridge geophysics and geochemistry under a single unified theory has been demonstrated. The mechanical, water and chemical energy has been combined for the analysis. Dual chemical osmosis and sorption in an unsaturated condition may have important engineering applications, such as nuclear waste disposal or biological tissue engineering, in which the function of a semi-permeable membrane exists. The new mathematical formulation presented in this paper provides a more accurate modelling tool for such engineering problems. Further research is needed to study the dual chemical osmosis influence on swelling rocks, given that clays and claystones have great swelling potential.

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