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Mixture-Coupling theory: a mathematical model of coupled dual chemical osmosis and sorption

Xiaohui Chen, Anna Cutting

School of Civil Engineering, University of Leeds, UK, X.CHEN@LEEDS.AC.UK

Aizhong Ding

College of Water Science, Beijing Normal University

ABSTRACT: Very low permeability geomaterials have been used widely as barriers for landfill or nuclear waste disposal. Such materials can act as an actual semipermeable membrane. Most recently, chemical osmosis & thermal osmosis have been found important in such membrane porous media, but the theoretical and mathematical development remains a challenge due to the complexity of couplings of multiple phases and components, which thereby presents a significant bundle for scientific understanding and engineering application. This paper provides a mathematical model for dual chemical osmosis and chemical reaction based on mixture coupling theory, extending Darcy's law with chemical osmosis and reaction. The modified Darcy's law can be applied in any chemical disturbed underground zone.

KEYWORDS: Mixture Coupling Theory, chemical osmosis, membrane porous media

LIST OF SYMBOLS

A, B, C (a,b,c): a, b, c appropriate integers of involved molecules of A, B, and C

\mathbf{I}_β velocity relative to solid, $\mathbf{I}_\beta = \tilde{\rho}_\beta(\mathbf{v}_\beta - \mathbf{v}_s)$; $\beta = w$ or c ;

\mathbf{J}_β is the diffusion flux of β

\mathbf{K} is the intrinsic permeability,

k_w is the relative permeability,

M_β is the mole mass

n_β is the mole of β

$n_{c_{A,R}}$ is the reaction amount of A

∇p is fluid pressure gradients.

r_{c_a} , r_{c_b} and r_{c_c} are reflection coefficient.

ΔS is the entropy change induced by chemical reaction

Greek symbols

γ is the entropy change of the whole system Ω

Ω is the subsystem

$\tilde{\rho}_\beta$ is the fluid density of β .

μ_w is the water's dynamic viscosity

1. INTRODUCTION.

Porous media is an important topic in Geotechnical Engineering. It controls fluid storage in aquifers, the movement of moisture through and under engineering structures, transport of pollutants in aquifers and the propagation of stresses under foundations of structures (Bear and Buchlin 1991). Soil permeability also has a decisive effect on the stability of foundations, seepage loss through embankments of reservoirs, drainage of subgrades, excavation of open cuts in water-bearing sands and rate of flow of water into wells (Nagaraj and Srinivasa 1994). The mathematical models which governs these physical processes are combinations of empirical laws such as Darcy's law, Fick's law, and Fourier's law and volume averaged conservations laws (Sullivan 2013).

In 1856, Henry Darcy investigated steady state unidirectional flow in a homogeneous and isotropic porous medium and discovered a proportionality between specific discharge, q , and the hydraulic gradient J . Darcy's law is a macroscopic law and so it is intended to be expressive over many pores and not just one single pore (Pant 2016).

The equation is given as follows.

$$q = -\frac{k}{\mu} \rho g J \quad (1)$$

Where μ is the dynamic viscosity of the fluid, ρ is the density of the fluid, g is the gravity acceleration, J is the hydraulic gradient and k is the specific permeability.

The specific permeability is the permeability of a porous medium to a specific fluid. Klinkenberg (1941) (Klinkenberg 1941) noted that if the fluid reacts with the core material, such as water may cause the clay to swell, then differences between the permeability of a medium can be expected. Furthermore, when a low pressured gas is flowing through the medium, the calculated permeability may be higher than the absolute. This is because, in liquid laminar flow, the layer of molecules in contact with and adjacent to the solid matrix walls is stationary (this is the same theory of flow in pipes). This is slightly different in gases at low pressures due to the larger mean free path that it causes and the reduced contact with the wall. This means that there is no friction loss at the walls and so the specific permeability is much higher. This theory is called gas slippage (Freeman, Moridis et al. 2010).

However, the transport of gas through porous media and therefore multiphase flow is out of the scope of this project and so the specific permeability is assumed to just be the permeability (Nield and Bejan 2006). Furthermore, it was noted by Muskat and Meres (1936) (Muskat and Meres 1936) that as long as Darcy's law is obeyed and the rate of flow is proportional to the pressure gradient, the permeability constant is a property of the medium and is independent of the fluid. Absolute permeability of porous rocks is an intrinsic property defined by the materials internal structure (Civan 2010). This absolute permeability applies to all liquids at laminar flow rates that are non-reactive to rock.

One of the biggest limitations to Darcy's law is that it is only applicable to laminar flow, this is because an assumption that

Darcy's law makes is that kinetic energy can be ignored, at higher flow velocities inertial flow is no longer negligible and therefore becomes a turbulent flow. Another limitation is that Darcy's law assumes that the fluid properties are constant (Brikowski 2015). Furthermore, Darcy's law does not contain sufficient information to solve time dependent problems. In order to do this, a mathematical expression of the principle of conservation of mass must be derived (Tyree and Zimmermann 2002).

In 1855, (around the same time, yet independently to Darcy) Adolf Fick established the equations of diffusion (Fick 1855, Fick 1995). According to this law, the transfer of salt and water occurring in a unit of time between two elements of space filled with two different solutions of the same salt must be directly proportional to the difference of concentrations and inversely proportional to the distance of the elements from one another (Philibert 2006).

Diffusion is the transport of compounds which arises because of random motion of the molecules (Perkins and Johnston 1963). It is a process that works to eliminate sharp discontinuities in concentration (Honrath, Matschke et al. 2017). The flux density, J , is the rate of mass transferred across a plane perpendicular to the direction of the mass flow per unit time, per unit area and is given by:

$$J = -D \frac{\partial C}{\partial x} \quad (2)$$

The diffusive coefficient D varies with temperature and molecular weight of the diffusing molecule. This is because the average speed of the random molecular movement is dependent on kinetic energy. As heat is added to the material, the temperature increases so that the thermal energy is converted to kinetic energy and thus allowing the molecules to move faster, this is turn allows for an increase in the rate of diffusion.

A solution is a homogenous mixture of two or more substances which form a single phase (solutes in porous media). Solute transport consists of two aspects, movement with the fluid and movement within it. The movement of the fluid relies on the fluids physical properties as well as the geometry and chemical properties of the surrounding solid. Movement within the fluid relies on the thermal motion which leads to molecular diffusion.

Diffusion is the process which a solute moves from areas of higher chemical potentials to areas of lower chemical potentials. This process is known as diffusions. Advection is the process by which dissolved solutes are carried along with the flowing groundwater.

Osmosis is a case of diffusion which involves the movement of water molecules across a partially permeable membrane. The solvent flows from an area of low solute concentrate to the region of high solute concentrate. This flow increases the fluid pressure in the area of high solute concentrate, this pressure change causes a countering hydraulic flow until the two opposing flows cancel each other an equilibrium is reached (Medved and Černý 2013). Osmosis is a colligative theory in that it does not depend on the specific nature of the solute, only its concentration (Borg 2003). Osmosis is the movement of water (or solvent) from a lower concentration of solute to a region of a higher concentrate of solute. Reverse osmosis, as the name suggests, works in reverse of this; where a pressure is applied to the region of a higher concentrate of solute to force the solvent to move across the membrane in the opposite direction as natural osmosis would allow. The

pressure that is applied to this must be high enough to overcome the osmotic pressure (Robinson 2005). The osmotic pressure is dependent on the solute concentration and so the higher the concentration of feed water, the higher the required pressure.

Mixture coupling theory (formally known as modified mixture theory), which was developed by (Heidug and Wong 1996), and substantially extended by Chen etc (Chen and Hicks 2013, Chen, Pao et al. 2013, Chen, Pao et al. 2016), is employed and further extended in this paper for chemical reaction. Darcy's law has been fundamentally extended by including in dual chemical osmosis and chemical reaction (e.g. sorption)

2. MATHEMATICAL DERIVATION

We select an arbitrary sub-region Ω with boundary Γ in a geological barrier and assume no solids move across Γ . A few assumption is made to simply the discussion: only two chemicals A and B present in the porous media, and $A+B=C$ as the secondary chemical. (2) A, B and C all have the capacity for chemical osmosis. (3) C does not precipitate and does not affect functions of the solid matrix.

Chemicals and water transport in porous media may induce entropy change of the local sub-region, which includes the friction between water body and the matrix of solid, and chemical reaction between A and B. The friction has been considered previously by many types of research and is one of the reason slows down the water transient flow, but the entropy change due to the chemical reaction and therefore the induced influence on water and chemical diffusion process has remained unclear. The dissipation caused by transport and reaction process may be summarized as (Katachalsky and Curran 1965)

$$0 \leq T\gamma = -\mathbf{I}_w \cdot \nabla \xi_w - \mathbf{I}_{c_A} \cdot \nabla \xi_{c_A} - \mathbf{I}_{c_B} \cdot \nabla \xi_{c_B} - \mathbf{I}_{c_C} \cdot \nabla \xi_{c_C} - T \cdot \Delta S_R \quad (3)$$

where $\mathbf{I}_\beta = \tilde{\rho}_\beta (\mathbf{v}_\beta - \mathbf{v}_s)$; $\beta = w$ or c , γ is the entropy change of the whole system Ω , $\tilde{\rho}_\beta$ is the fluid density of β . Note here, in the equation (3), theoretically, $T\gamma$ can be zero if the dissipation introduced by chemical reaction ($T \cdot \Delta S_R$) equals other dissipation processes ($-\mathbf{I}_w \cdot \nabla \xi_w - \mathbf{I}_{c_A} \cdot \nabla \xi_{c_A} - \mathbf{I}_{c_B} \cdot \nabla \xi_{c_B} - \mathbf{I}_{c_C} \cdot \nabla \xi_{c_C}$).

If a simple chemical reaction is considered to be



where a, b, c are appropriate integers of involved molecules A, B, and C, respectively. ΔS is the entropy change induced by chemical reaction. \mathbf{I}_β can be linked with mole n_β through

$$\mathbf{I}_\beta = \tilde{\rho}_\beta (\mathbf{v}_\beta - \mathbf{v}_s) = \frac{m_\beta}{V} (\mathbf{v}_\beta - \mathbf{v}_s) = \frac{n_\beta M_\beta}{V} \quad (5)$$

where n_β is the mole of β and M_β is the mole mass.

Assuming the reaction amount of A is $n_{c_{A,R}}$, and by using (4), the reaction amount of B and C may be described as

$$n_{c_{C,R}} = \frac{c}{a} n_{c_{A,R}}, n_{c_{B,R}} = \frac{b}{a} n_{c_{A,R}} \quad (6)$$

therefore, the equation (3) becomes

$$0 \leq T\gamma = -\mathbf{I}_w \cdot \nabla \xi_w - (\mathbf{I}_{c_A} - \mathbf{I}_{c_{A,R}}) \cdot \nabla \xi_{c_A} -$$

$$(\mathbf{I}_{c_B} - \frac{b}{a} \mathbf{I}_{c_{A,R}}) \cdot \nabla \xi_{c_B} - (\mathbf{I}_{c_C} + \frac{c}{a} \mathbf{I}_{c_{A,R}}) \cdot \nabla \xi_{c_C} - T \cdot (\frac{n_{c_{A,R}}}{a}) \Delta S_R \quad (7)$$

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

$$\mathbf{J}_\beta = \tilde{\rho}_\beta (\mathbf{v}_\beta - \mathbf{v}_f) \quad (8)$$

the relationship between \mathbf{I}_β and \mathbf{J}_β is:

$$\mathbf{J}_\beta = \mathbf{I}_\beta - \tilde{\rho}_\beta (\mathbf{v}_f - \mathbf{v}_s) \quad (9)$$

$$0 \leq T\gamma = -\mathbf{u}_D \cdot \nabla p_p - \mathbf{J}_{c_A} \cdot \nabla (\xi_{c_A} - \xi_w)$$

$$- \mathbf{J}_{c_B} \cdot \nabla (\xi_{c_B} - \xi_w) - \mathbf{J}_{c_C} \cdot \nabla (\xi_{c_C} - \xi_w) - T \cdot (\frac{n_{c_{A,R}}}{a}) \Delta S_R \quad (10)$$

In the equation(10), there is four major driving force: ∇p_p is for water flow, $\nabla (\xi_{c_A} - \xi_w)$ is for diffusion flux of chemical A, $\nabla (\xi_{c_B} - \xi_w)$ is for diffusion flux of chemical B, $\nabla (\xi_{c_C} - \xi_w)$ is for diffusion flux of chemical C, and ΔS_R represents instant chemical reaction. If the chemical reaction is a kinetic reaction (time dependent), then ΔS_R is replaced by ∇S_R .

By using phenomenological equations to give the linear dependence of driving force and corresponding flux, equation (10) can be further derived as

$$\rho_f \mathbf{u}_D = - \left(\frac{L_{11}}{\rho_f} \right) \nabla p_p - L_{12} \nabla (\xi_{c_A} - \xi_w)$$

$$- L_{13} \nabla (\xi_{c_B} - \xi_w) - L_{14} \nabla (\xi_{c_C} - \xi_w) - L_{15} \nabla S_R \quad (11)$$

By linking chemical potential with fluid pressure (Chen and Hicks 2013) as follows

$$\nabla (\xi_{c_A} - \xi_w) = (v_{c_A} - v_w) \nabla p_p + \frac{1}{C_w} \frac{\partial \xi_{c_A}}{\partial C_{c_A}} \nabla C_{c_A} \quad (12)$$

$$\nabla (\xi_{c_B} - \xi_w) = (v_{c_B} - v_w) \nabla p_p + \frac{1}{C_w} \frac{\partial \xi_{c_B}}{\partial C_{c_B}} \nabla C_{c_B} \quad (13)$$

$$\nabla (\xi_{c_C} - \xi_w) = (v_{c_C} - v_w) \nabla p_p + \frac{1}{C_w} \frac{\partial \xi_{c_C}}{\partial C_{c_C}} \nabla C_{c_C} \quad (14)$$

Therefore, equation (11) can be further derived as

$$\mathbf{u}_D = - \frac{\mathbf{K} \mathbf{k}_{tw}}{\mu} \left(\begin{array}{l} \nabla p_p - r_{c_A} \frac{\rho_f}{C_w} \frac{\partial \xi_{c_A}}{\partial C_{c_A}} \nabla C_{c_A} - r_{c_B} \frac{\rho_f}{C_w} \frac{\partial \xi_{c_B}}{\partial C_{c_B}} \nabla C_{c_B} \\ - r_{c_C} \frac{\rho_f}{C_w} \frac{\partial \xi_{c_C}}{\partial C_{c_C}} \nabla C_{c_C} - r_{c_R} \nabla S_R \end{array} \right) \quad (16)$$

where μ_w is the water's dynamic viscosity, \mathbf{K} is the intrinsic permeability, \mathbf{k}_{tw} is the relative permeability, r_{c_A} , r_{c_B} and r_{c_C} are reflection coefficient.

Equation (10) shows a further extension of Darcy's Law, with consideration of dual chemical osmosis, and chemical reaction. The terms $r_{c_A} \frac{\rho_f}{C_w} \frac{\partial \xi_{c_A}}{\partial C_{c_A}} \nabla C_{c_A}$, $r_{c_B} \frac{\rho_f}{C_w} \frac{\partial \xi_{c_B}}{\partial C_{c_B}} \nabla C_{c_B}$ and

$-r_{c_C} \frac{\rho_f}{C_w} \frac{\partial \xi_{c_C}}{\partial C_{c_C}} \nabla C_{c_C}$ represent the osmotic influence of chemical A,

B, and C, respectively, and in which The combination of these three flow will finally have an influence on ∇p_p , thus affect water flow. Additionally, chemical reaction term $r_{c_R} \nabla S_R$ further influences the water flow.

This equation provides a theoretical framework for the experimental study of smarter control of flow through chemical osmosis and chemical reaction. It has extensive potential industrial applications such as nuclear waste disposal, landfill, CCS and Cancer research, especially if the scientific concept is based on membrane porous media.

4. CONCLUSION

The mathematical equation derived from this research has fundamental changed Darcy's Law through the incorporation of microscope chemical osmosis. This equation describes a more realistic prediction of water transport in a geological barrier.

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