Mathematical model of coupled dual chemical osmosis based on mixture-coupling theory

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A B S T R A C T

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.

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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 (Sun, Wu, Shi, & Wu, 2016). 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 (Chen, Pao, Thornton, & Small, 2016; Santana, 2016). 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.

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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 (1943) and Biot (1962,1972), in which considerable research has been done, including the development of hydro-mechanical coupled models, and theoretical analysis of thermal and/or chemo coupling Seetharam, Thomas, & Cleall, 2007); ((2); Yasuhara, Kinoshita, Ogata, Cheon and Kishida (2016) mixture theory approach, which was firstly developed by Truesdell (1957) and further extended by Bowen (1976, 1980, 1984), maintains the individuality of the solid and fluid phases (Bowen, 1984; Truesdell & Toupin, 1960), with recent contribution by Rajagopal etc. (Humphrey & Rajagopal, 2002; Humphrey & Rajagopal, 2003; Rajagopal, 2007; Rajagopal & Tao, 1995; Rajagopal, Wineman, & Gandhi, 1986). A comprehensive review of this approach has been completed by Atkin and Craine (1976). This approach has the difficulties of obtaining information on the interaction between the phases as discussed by Rajagopal et al. (1986); and (3) Mixture-Coupling theory approach, which combines the advantages of both former approaches, provides a smooth link between geophysics and geochemistry (Chen & Hicks, 2012,2009a, 2010; Chen et al., 2016; Heidug & Wong, 1996). Mixture coupling theory was formally known as Modified Mixture Theory and first proposed by Heidug and Wong (1996) for saturated rocks. It was later extended to unsaturated conditions and non-isothermal conditions (Chen, 2010; Chen & Hicks, 2012, 2009b, 2013). 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 Katsube and Carroll (1987), it is necessary to rename it as Mixture Coupling Theory (Chen et al., 2016), 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 Chen and Hicks (2013). 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 (Laloui, Klubertanz, & Vulliet, 2003). Mixture theory has difficulties in obtaining information on the interactions between solid/fluid phases, and also to deal with the coupling of chemicals (Bowen, 1984; Truesdell & Toupin, 1960). 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 (Chen & Hicks, 2013; Chen et al., 2016, 2013).

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 (Chen & Hicks, 2010, 2018; Heidug & Wong, 1996).

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 (Neuman, 1975; Safai & Pinder, 1979).

2.1. Flux definition

The flux is given as:

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

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 ($\beta = w$) or chemical ($\beta = c$) 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 Eq. (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.