Journal of Contaminant Hydrology 138-139 (2012) 40–59

Contents lists available at SciVerse ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

Review article

Critical review of coupled flux formulations for clay membranes based on nonequilibrium thermodynamics

Michael A. Malusis [a,*], Charles D. Shackelford [b,1], James E. Maneval [c,2]

[a] Department of Civil and Environmental Engineering, Bucknell University, Lewisburg, PA 17837, USA
[b] Department of Civil and Environmental Engineering, Colorado State University, 1372 Campus Delivery, Fort Collins, CO 80523, USA
[c] Department of Chemical Engineering, Bucknell University, Lewisburg, PA 17837, USA

ARTICLE INFO

Article history:
Received 25 January 2012
Received in revised form 1 June 2012
Accepted 5 June 2012
Available online 23 June 2012

Keywords:
Clay membrane
Coupled flux
Diffusion
Osmosis
Solute transport

ABSTRACT

Extensive research conducted over the past several decades has indicated that semipermeable membrane behavior (i.e., the ability of a porous medium to restrict the passage of solutes) may have a significant influence on solute migration through a wide variety of clay-rich soils, including both natural clay formations (aquitards, aquicludes) and engineered clay barriers (e.g., landfill liners and vertical cutoff walls). Restricted solute migration through clay membranes generally has been described using coupled flux formulations based on nonequilibrium (irreversible) thermodynamics. However, these formulations have differed depending on the assumptions inherent in the theoretical development, resulting in some confusion regarding the applicability of the formulations. Accordingly, a critical review of coupled flux formulations for liquid, current, and solutes through a semipermeable clay membrane under isothermal conditions is undertaken with the goals of explicitly resolving differences among the formulations and illustrating the significance of the differences from theoretical and practical perspectives. Formulations based on single-solute systems (i.e., uncharged solute), single-salt systems, and general systems containing multiple cations or anions are presented. Also, expressions relating the phenomenological coefficients in the coupled flux equations to relevant soil properties (e.g., hydraulic conductivity and effective diffusion coefficient) are summarized for each system. A major difference in the formulations is shown to exist depending on whether counter diffusion or salt diffusion is assumed. This difference between counter and salt diffusion is shown to affect the interpretation of values for the effective diffusion coefficient in a clay membrane based on previously published experimental data. Solute transport theories based on both counter and salt diffusion then are used to re-evaluate previously published column test data for the same clay membrane. The results indicate that, despite the theoretical inconsistency between the counter-diffusion assumption and the salt-diffusion conditions of the experiments, the predictive ability of solute transport theory based on the assumption of counter diffusion is not significantly different from that based on the assumption of salt diffusion, provided that the input parameters used in each theory are derived under the same assumption inherent in the theory. Nonetheless, salt-diffusion theory is fundamentally correct and, therefore, is more appropriate for problems involving salt diffusion in clay membranes. Finally, the fact that solute diffusion cannot occur in an ideal or perfect membrane is not explicitly captured in any of the theoretical expressions for total solute flux in clay membranes, but rather is generally accounted for via inclusion of an effective porosity, n_e, or a restrictive tortuosity factor, τ_r, in the formulation of Fick's first law for diffusion. Both n_e and τ_r have been correlated as a linear function of

* Corresponding author. Tel.: +1 570 577 1683; fax: +1 570 577 3514.
E-mail addresses: mam028@bucknell.edu (M.A. Malusis), shackel@engr.colostate.edu (C.D. Shackelford), maneval@bucknell.edu (J.E. Maneval).
[1] Tel.: +1 970 491 5051.
[2] Tel.: +1 570 577 1669.

0169-7722/$ – see front matter
doi:10.1016/j.jconhyd.2012.06.003

membrane efficiency. This linear correlation is supported theoretically by pore-scale modeling of solid–liquid interactions, but experimental support is limited. Additional data are needed to bolster the validity of the linear correlation for clay membranes.

Contents

1. Introduction

The ability of clays to act as semipermeable membranes that inhibit the passage of solutes while allowing relatively unimpeded migration of the solvent (water) is well recognized and has been the subject of extensive research over the past several decades. For example, numerous experimental studies have been conducted to evaluate the effects of membrane behavior in clay-rich soils on agricultural processes (e.g., salt infiltration and soil salinization), groundwater flow through confining beds, salt-water intrusion, and mechanical behavior (Barbour, 1986; Barbour and Fredlund, 1989; Cey et al., 2001; Di Maio, 1996; Garavito, 2005; Garavito et al., 2007; Greenberg, 1971; Hanshaw, 1962; Keijzer, 2000; Keijzer et al., 1997; Kemper and Rollins, 1966; Kharaka and Berry, 1973; Kharaka and Smalley, 1976; McKelvey and Milne, 1960; Neuzil, 1986; Olsen, 1969; Rahman et al., 2005; Young and Low, 1965). In addition, recent experimental studies have indicated the existence of membrane behavior in engineered clay barriers used for hydraulic containment applications (e.g., landfills, surface impoundments, etc.), such as geosynthetic clay liners (GCLs), compacted clay liners, and soil-bentonite backfills for vertical cutoff walls (Di Emidio, 2010; Evans et al., 2008; Henning, 2004; Henning et al., 2006; Kang, 2008; Kang and Shackelford, 2009, 2010, 2011; Malusis, 2001; Malusis and Shackelford, 2002a,2002b; Malusis et al., 2001; Mazzieri et al., 2003, 2005, 2010; Saindon and Whitworth, 2005; Shackelford, 2012; Shackelford and Lee, 2003; Van Impe, 2002; Yeo, 2003; Yeo et al., 2005). Collectively, this extensive body of research has demonstrated that significant membrane behavior is possible in clay soils, particularly those soils rich in high swelling smectite minerals, such as bentonite (Di Emidio, 2010; Kang and Shackelford, 2010; Kemper and Quirk, 1972; Kemper and Rollins, 1966; Malusis and Shackelford, 2002a; Milne et al., 1964; Shackelford, 2012; Shackelford et al., 2003; Yeo et al., 2005).

In addition to the aforementioned experimental studies, several theoretical studies have been devoted to characterizing liquid flow and solute transport through clay membranes based on coupled flux theory derived from principles of nonequilibrium (irreversible) thermodynamics (Bader and Kooi, 2005; Dominijanni, 2005; Dominijanni and Manassero, 2012a; Garavito et al., 2002; Greenberg, 1971; Greenberg et al., 1973; Groenevelt and Bolt, 1969; Groenevelt and Elrick, 1976; Groenevelt et al., 1978, 1980; Kooi et al., 2003; Lu et al., 2004; Malusis, 2001; Malusis and Shackelford, 2002c; Manassero and Dominijanni, 2003; Mitchell et al., 1973; Olsen et al., 2000; Soler, 2001; Van Impe, 2002; Van Impe et al., 2003, 2006; Yeung, 1990; Yeung and Mitchell, 1993). However, the coupled flux formulations in these studies have differed, and the differences have not been elucidated in a comprehensive manner, which can lead to confusion over the validity or applicability of the various formulations. As a result, a critical review of these formulations was undertaken with the goal of explicitly resolving the differences among the formulations and illustrating the significance of these differences from both theoretical and practical perspectives.