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Research Paper

An analytical model for diffusion of chemicals under thermal effects in semi-infinite porous media

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ABSTRACT

An analytical solution for one-dimensional diffusion of chemicals under coupled chemical and thermal potentials is presented. The theoretical formulation considered includes heat conduction and chemical diffusion due to both molecular and thermal diffusion potentials. Laplace transformation technique has been used to derive the analytical solution to the problem in a semi-infinite domain. The results obtained by the proposed analytical solution have a good agreement with those obtained from the laboratory tests of thermal diffusion of a salt solution in a compact clay. Comparisons with the numerical model were also carried out to investigate the effects of transient heat conduction and temperature-dependency of diffusion coefficient on the chemical transport due to a thermal gradient. An application of the model to study the effects of thermal diffusion on chemical transport in a compacted clay liner (CCL) is presented. The results show that the base concentration and flux of the chemical in the CCL increases with the increase of the temperature and Soret coefficient. The 40-year bottom fluxes for the case with thermal diffusion are 2–11 times greater than the case with only molecular diffusion for a 0.6 m compacted clay liner. Based on the results achieved, thermal diffusion demonstrates considerable effect in the landfill design. In the simulation scenario with $S_T = 5 \times 10^{-2}$ 1/K, the base concentration and the flux of the chemical at 100 years is 1.5 times and 8 times larger, respectively than those obtained from the simulation without considering thermal diffusion. Using the analytical model presented, a series of dimensionless design charts are presented that can be used to estimate the thickness of the CCL, under non-isothermal conditions. The proposed analytical solution provides a simple method for the verification of alternative numerical models, evaluation of groundwater/soil remediation methods and preliminary design of landfill clay liners.

1. Introduction

Compacted Clay Liners (CCLs) are engineered barriers that are used as the bottom liner systems in landfills due to their low permeability and relatively good compatibility with the leachate contaminants [25,28,29]. CCLs are the main landfill liner materials used in China, where approximately 90% of the municipal solid wastes are disposed in the landfills. The standards for the design of landfill liner systems indicate a minimum of 2 m CCL or a composite liner consisting of a geomembrane (GM) and a 75 cm CCL in China [20] and a GM and a 60 cm CCL in the US [12].

It has been shown that the molecular diffusion is the main mechanism for the transport of leachate contaminant in the clay barriers due to the low hydraulic conductivity (e.g. $<10^{-7}$ cm/s) of the clays and low leachate head (e.g. <30 cm) in well-constructed/-controlled landfills [13,14,28,41,29]. Thermal processes in landfills can be observed due to biodegradation of municipal solid waste (MSW) or the heat generation induced by hydration of the incinerated bottom ash [29,30]. High temperature values (50–70 °C) have been reported in many landfills [37,29]. Reactive wastes, such as wastes from aluminum production, have been also observed to produce high temperature values (more than 100 °C) in the landfill and in some cases even up to 150 °C have been reported [5].

It is well established that under non-isothermal conditions, a temperature gradient can induce mass flow due to thermal diffusion, i.e. the Soret–Ludwig effect or Soret effect [40,26,21]. The Soret coefficient is defined as the ratio of the thermal diffusion

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Nomenclature

η	viscosity of solvent
A	temperature gradient of compacted clay liner
B	temperature in the leachate
C_i	background concentration in compacted clay liner
C_N	relative concentration of leachate constituent
C_0	concentration in the leachate
D^0	tracer diffusion coefficient in pure water
D^*	effective diffusion coefficient of compacted clay liner
F_N	dimensionless flux at base of compacted clay liner
L	thickness of compacted clay liner
M	dimensionless parameter regarding temperature difference between two sides of compacted clay liner
n	porosity of compacted clay liner
R_d	retardation factor of the compacted clay liner
S_T	Soret coefficient of the compacted clay liner
T	temperature of the compacted clay liner
T_r	reference temperature
T_R	dimensionless time factor

coefficient to the molecular diffusion coefficient (K^{-1}). It is nted that in addition to the direct mass flux due to the thermal diffusion, temperature has an influence on the molecular diffusion and the effective diffusion coefficient. This phenomenon in aqueous systems has been well studied and established in the literature. Several studies have been conducted on the thermal diffusion in electrolyte solutions (e.g. [35,17]. At ambient temperature, the Soret coefficient has been reported in the order of 10^{-2}–10^{-3} (K^{-1}) for electrolyte solutions [16]. It has been also found that the Soret coefficient is dependent on the concentration of the solution [17,11]). Soret coefficient (thermal diffusion coefficient) is usually small in dilute solutions but it is largest for solutes with different molecular weights or for highly non-ideal solutions [10]. Based on a hydrodynamic approach, Agar et al. [3] provided a theoretical formulation for standard heat of transport of ions in infinite dilute electrolyte solution at ambient temperature. The theoretical approach suggested analogies between the heat of transport and dielectric properties of the solutions. Accordingly, the Soret coefficient is a square function of ionic valance and a function of self diffusion coefficient of ions. The values of Soret coefficients for aqueous solutions are also temperature dependant [10,16]. Based on theoretical formulation of thermal diffusion (e.g. [32,38], the effect of thermal diffusion depends on thermal gradient applied in the domain and the magnitude of heat transport.

Experimental studies have shown the importance of thermal effects on the diffusion of chemicals in electrolyte solutions (e.g. [17]. Rosanne et al. [26,27] also reported an experimental comparison on thermal diffusion of NaCl solution in glass powder, mica and argillite clay. They found that the Soret coefficients for mica and glass powder are very close to the values reported for the Soret coefficient of NaCl in water. However, the values corresponding to the argillite clay was found to be five times larger than the value in free water, attributing to the electrostatic interaction with clay surfaces [27]. The results of non isothermal diffusion experiment by Rosanne et al. [26,27] show that the solute transfer is enhanced by thermal diffusion and the Soret coefficients range between 5×10^{-3} and 1.3×10^{-2} (K^{-1}). Theoretical formulation of the diffusion of multiple chemicals under the effects of temperature has also been presented and applied numerically to study the diffusion of chemicals in compacted clays [32,38,39].

Analytical solutions for contaminant diffusion in soils [6,19,43] and composite liners [12,9,44,45] have been presented in the literature which consider the molecular diffusion and adsorption of contaminants in the barriers. However, the analytical solutions presented for contaminant diffusion neglect the effect of temperature and the process of thermal diffusion. To the knowledge of the authors, no analytical solution has been presented which consider the processes of molecular diffusion and thermal diffusion together to study the contaminant transport in liner systems.

This paper presents an analytical solution for non-isothermal diffusion of chemicals in a semi-infinite porous medium. The proposed analytical model considers the steady-state heat transfer via conduction and the chemical transport due to both molecular and thermal diffusion potentials. The results of the proposed analytical model are compared with those obtained from a series of laboratory tests reported in the literature. The analytical solution is also tested against a coupled heat, moisture and chemical numerical model [38,39]. The model developed is applied to study the long term chemical diffusion in a compacted clay liner, used to contain contaminants in landfills. The application example demonstrates the impact of thermal diffusion on the transport process and the use of the solution for CCL design. Effort has been made to produce a series of dimensionless diagrams to assist with the design of the clay liner when thermal effects are in place.

2. Theoretical formulation and analytical solution

A coupled theoretical formulation of heat conduction and chemical diffusion in saturated porous media is considered in developing the analytical solution. Heat conduction is assumed to be under steady-state condition while a transient chemical diffusion under chemical and thermal potentials is considered. The assumption of steady-state heat conduction is based on the fact that the temperature profile in the domain reaches equilibrium more quickly than the case for chemical transport. This has been observed both in experimental studies of thermal diffusion in aqueous solution [17] and in the numerical simulations [32,38]. A schematic diagram of the proposed model is shown in Fig. 1.

The general governing equation for chemical diffusion in a multicomponent chemical system under coupled electrochemical and thermal potentials, as presented by Thomas et al. [38], can be simplified for the case of one dimensional diffusion of a single chemical, as:

$$R_d \frac{\partial C}{\partial t} = D^* \frac{\partial^2 C}{\partial z^2} + S_T D^* \frac{\partial}{\partial z}\left(C \frac{\partial T}{\partial z}\right) \tag{1}$$

where C is the chemical concentration. R_d is the retardation factor and t represents the time. D^* is the effective diffusion coefficient

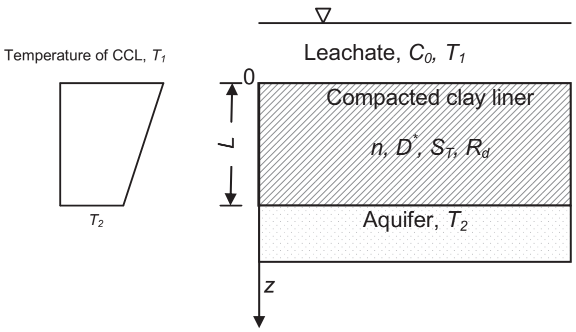

Fig. 1. Schematic diagram of the proposed mathematical model.