

DIFFUSION OF CHEMICALS UNDER UNSTEADY-STATE HEAT TRANSFER IN SATURATED POROUS MEDIA

Jimmy Synclair KENHAGO WATIA¹, Elie SIMO^{2*}

¹Ecole de géologie et d'exploitation minière de Ngaoundéré, Département.: Management Global et développement durable, Université de Ngaoundéré – Cameroon.

²Physics Department, Laboratory of Energy and Environment -Faculty of Science, University of Yaounde I, P.O. Box 812 Yaounde – Cameroon.

* Corresponding author: esimotc@yahoo.com

Abstract.

A numerical solution for one-dimensional diffusion of chemicals under coupled chemical and thermal potentials is presented. The theoretical formulation considered includes thermal conduction and chemical diffusion due to molecular and thermal diffusion potentials. The investigation quantifies the spatio-temporal variations of the solute and studies the effects of the associated characteristic parameters. Established nonlinear and variable coefficient equations describing heat and mass transfer processes are solved using the MATLAB pdepe solver. The numerical prediction of solute movement is compared to the reference analytical solution from the literature and good performances are presented. Comparisons with the steady state heat transfer model were also carried out to study the influence of the Soret effect and the temporal variation of temperature on chemical transport due to a thermal gradient. The analysis presented shows that the Soret effect significantly influences solute transport in unsteady regime. Compared to this regime, solute transfer responses with stationary thermal transfer suggest that the solute present in a subspace can be underestimated or overestimated as a function of time. It was also found that a temporal variation in the temperature of the medium affects the migration of solutes in the medium. For example, for an initial concentration of the solute at the surface $C_0 = 100 \text{ mol/m}^3$, the concentration gap between the two regimes can go up to 8 mol/m^3 . Similarly, an increase in average soil temperature induces rapid movement of solute in the domain. A large difference is observed between the forecasts in the steady and unsteady heat transfer regime when the average temperature increases from 323°K to 373°K . So, for an initial concentration $C_0 = 100 \text{ mol/m}^3$; the concentration at a depth of 0.5m at the 40-years date is 45.58 mol/m^3 and 60.67 mol/m^3 for the case of thermal diffusion in steady state with $T_m = 323^\circ\text{K}$ and $T_m = 373^\circ\text{K}$, respectively. However in unsteady regime, at the same position and on the same date, the concentration is 49.74 mol/m^3 and 73.86 mol/m^3 with $T_m = 323^\circ\text{K}$ and $T_m =$

373 °K, respectively. From the present numerical study, we observed that the temperature profiles increase with increasing initial surface concentration.

Keywords: Molecular diffusion, Soret effect, Unsteady regime, Porous medium, Heat transfer, Coupled problem

1. Introduction

Composite liners are widely used in modern municipal solid waste landfills as essential barrier structures to isolate the pollutants in landfill leachates from the external natural environment. Even though intact geomembranes (GMBs), the important components of composite liners, are nearly impenetrable by leachates, they could be readily diffused through by some organic pollutants (e.g., volatile organic compounds (VOCs)) (Chao et al., 2007). Moreover, organic pollutants are generally toxic even at low concentration compared to many inorganic pollutants (Edil, 2003; Xie et al., 2015a). Thus, studying the transport of organic pollutants through landfill composite liner is of great significance for rational design and barrier performance assessment.

Molecular diffusion is broadly recognized as one of the dominant transport mechanisms of pollutants in composite liner system. Plenty of pure diffusion analytical models have been proposed to investigate this issue (Chen et al., 2019; Pu et al., 2020; Qiu et al., 2021; Xie et al., 2015b). However, the transport mechanism of pollutant is diverse and complicated. Apart from molecular diffusion, there are advection, adsorption, biodegradation and thermal diffusion etc. that may also be involved (Chen et al., 2015; Feng et al., 2019a, 2019b; Lu et al., 2021; Lu and Feng, 2022; Pu et al., 2018, 2021; Yan et al., 2021).

In practice, there usually exist defects in GMBs, such as holes, wrinkles and seams due to large construction machinery, solar radiation and insufficient overlaps. Landfill leachates could break through GMBs via these defects by advection. Thus, some diffusion–advection models were also developed (Feng et al., 2019b; Xie et al., 2015a, 2018). For example, Xie et al. (2010, 2011) proposed a quasi-steady state analytical solution for pollutants diffusion and advection through GMB/CCL (note: CCL is compacted clay liner) and GCL/SL composite liners. Xie et al. (2015a) then extended this solution to GMB/GCL/SL composite liner system. Feng et al. (2019a, 2019b) further presented a transient solution to diffusion–advection transport of pollutant in the three-layer composite liner system. However, all these models assume that the composite liner works in an isothermal environment. Indeed, these models do not take into account the impact of thermodiffusion on the movement of solutes in coating systems.

Actually, there generally exists temperature gap between the leachate heaping on the geomembrane and the bottom surface of modern landfill composite liners (Rowe, 2012). Thus, the effect of thermodiffusion is of growing concern for the transport issue in landfills (Engelhardt et al., 1997; Leaist and Lv, 1990; Rahman and Saghir, 2014). On this topic, Xie and his coauthors (Xie et al. 2015c; Yan et al., 2020) presented a transport model suitable for monolayer porous media. Moreover, Peng et al. (2020, 2021, 2023) proposed transport models for organic pollutants in GMB/CCL and GMB/GCL/SL composite liners. These models chemical diffusion in porous media consider the molecular diffusion, thermodiffusion,

advection, degradation and adsorption of chemical. However, the solutions presented above for chemical diffusion neglect the effect of a thermally coupled process. The solutions proposed assumes a constant diffusion coefficient. However, temperature effects on the diffusion coefficients are not negligible. As an example, the experimental results of chemical diffusion of ionic species in a clay soil at elevated temperature indicated a strong influence on enhancing the chemical transport process as the result of temperature-dependency of the diffusion coefficient (Mon et al., 2016; Rosanne et al., 2003). Analytical solutions to the one-dimensional coupled molecular and thermal diffusions of chemical in saturated porous media were presented (Jiang et al., 2023; Yan et al., 2020), and consider the effects temperature dependency of diffusion coefficient under steady-state heat transfer. The transient behavior of heat conduction is not taken into account.

This article presents a new coupled model of solute transport and thermal transport in a finite porous medium. The numerical method is adopted to derive a solution. Solute thermal transport governed by molecular and thermal diffusion potentials in which the heat transfer process is steady-state, and solute thermal transport using steady-state heat transfer are discussed. The similarities and differences between the different approaches are highlighted. The developed model is applied to the study of long-term chemical diffusion in a compacted clay liner, used to contain contaminants in landfills.

2. Materials and methods

It is reasonable to characterize composite coatings as porous support materials (fig.1). For this, they present a risk of soil and subsoil pollution by chemical substances such as petroleum derivatives. Indeed, due to their porosity, these coatings can absorb pollutants until their pores are saturated, which can lead to contamination of the surrounding environments. The absorption of chemicals in composite coatings is largely influenced by the mechanism of capillary suction. This absorption process is described by Fick's law, which explains the movement of chemicals molecules through the material. Fick's law can be supplemented by the inclusion of an external transport flux vC , which is responsible for moving molecules at a certain average speed v . In this context, the Fick equation is written:

$$J = -D\nabla C + vC \quad (1)$$

Here, C represents the chemical concentration at a point at time t , D is the effective diffusion coefficient of the pollutant or the effective diffusivity and J the flux.

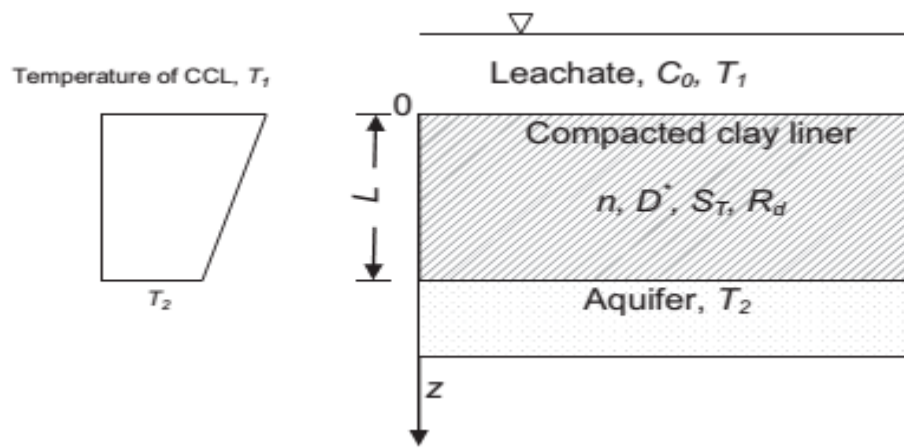


Fig. 1.Schematic diagram of the proposed mathematical model.

The thermodynamics of irreversible processes plays an essential role in determining the transport force responsible for the movement of molecules of pollutants at a speed v . According to the Nernst-Einstein equation, this transport force is related to the Boltzmann constant, temperature and diffusivity by:

$$\frac{v}{D} = \frac{F}{k T} \quad (2)$$

Where k is the Boltzmann constant, T the temperature and F the transport force.

Therefore, Fick's equation (1) can be modified to include this transport force. We get a more general expression:

$$J = -D \nabla C + \frac{D}{K T} F C \quad (3)$$

When considering the non-isothermal system with a temperature gradient, it is important to take into account the thermomigration effect. Thermomigration is a phenomenon that occurs when a substance migrates through a porous medium due to a temperature gradient. This process occurs due to the difference in mobility of molecules within the porous medium as a function of temperature. When there is a temperature gradient within the porous medium, the molecules of the substance move from areas of high temperature to areas of lower temperature. This happens because higher temperature molecules have higher kinetic energy, which allows them to move more easily through the pores and interstices of the porous medium. However, it is important to note that thermomigration only occurs if there is an interaction between the substance and the porous medium. This interaction can be caused by capillary forces, solubility effects or other chemical interactions defined by:

$$F = -K T S_T \nabla T \quad (4)$$

Where S_T is called Soret's coefficient.

Thus equation (3) becomes:

$$J = -D \nabla C - S_T D C \nabla T \quad (5)$$

In non-steady state, that is to say when the flow at each point varies with time, it is necessary to complete the Fick equation with a balance equation. For conservative species, this is the continuity equation:

$$\frac{\partial c}{\partial t} = -\nabla J \quad (6)$$

By combining equations (5) and (6) we obtain the following diffusion equation:

$$\frac{\partial c}{\partial t} = \nabla(D\nabla C) + \nabla(S_T D C \nabla T) \quad (7)$$

The pollutant is assumed to be inert, there are no wells or additional points below the source and the longitudinal and lateral components of the flow speed are assumed to be zero. The model simulates the concentration along a one-dimensional flow in a finished heterogeneous porous medium, where migration is considered to be in the vertical direction, that is to say the axis of the z (from $z=0$ to $z=L$). Initially, the porous field is not free from polluting, which means that there is a certain concentration in the field before the injection of the substance. A constant and uniform source of entry enters the upper end of the porous domain. Large quantities of pollutants are transported through this area, during which polluting masses diffuse, resulting in a decrease in the maximum concentration with the position.

If we consider one-dimensional transfer of the pollutant, this master equation (7) is transformed into

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left(D(T) \frac{\partial c}{\partial z} \right) + \frac{\partial}{\partial z} \left[S_T D(T) C \frac{\partial T}{\partial z} \right] \quad (8)$$

z measures the penetrating depth of the pollutants in the media.

Now, we consider the restrictive case where the diffusion coefficient is constant. The chemical penetrating the liner under steady-state heat transfer is described by the following equation in one dimension:

$$\frac{\partial c}{\partial t} = D_0 \frac{\partial^2 c}{\partial z^2} + G D_0 S_T \frac{\partial c}{\partial z} \quad (9)$$

Where G the temperature gradient dependent only on the boundary conditions of the problem.

Thus, Eq. (9) corresponds to the case where the diffusivity constant. This equation was used by xie and coworkers (Xie et al., 2015c) to study the long term chemical diffusion in a compacted clay liner. All calculations described above have been performed with the assumption that the transport coefficients (diffusivities, Soret coefficients, etc.) are independent of the concentration of the transferred species and temperature. While the dependence of transport coefficients on concentration can be ignored for dilute solutions, the temperature dependences of diffusion coefficients may be significant. A linear description of temperature dependency of the selfdiffusion coefficient is proposed based on experimental data by Harris and Woolf (1980):

$$D_T = D_0(MT + N) \quad (10)$$

The constants M and N are approximated by the values

$$M = \frac{1}{40} \text{ and } N = -\frac{255}{40} \quad (11)$$

These linear relationship between the diffusion coefficient and temperature (D_T) is compared with experimental data by Harris and Woolf (1980). The diffusivity for the chemical at the ambient temperature 295 K equals to $D_0 = 10^{-10} \text{ m}^2/\text{s}$.

Substituting Eq. (10) into Eq. (8), the diffusion of chemicals in saturated porous media under unsteady-state heat transfer can be presented as:

$$\frac{\partial C}{\partial t} = D_0 \frac{\partial}{\partial z} \left[(MT + N) \left(\frac{\partial C}{\partial z} + S_T C \frac{\partial T}{\partial z} \right) \right] \quad (12)$$

The solute transport is coupled to the heat flow phenomena. The thermal model is based on the principle of heat transfer through conduction. Thus, the heat transfer is described based on the Fourier's law as:

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left(D_T \frac{\partial T}{\partial z} \right) \quad (13)$$

where D_T is thermal diffusion coefficient.

In the scope of this study, the heat transfer is assumed to be under unsteady-state condition whilst a transient chemical diffusion under concentration and thermal potentials is considered (Eq. 12). The transient heat transfer hypothesis is based on the fact that in a diffusion-dominated system, the domain temperature profile and chemical distribution (when mass transport is diffusion-dominated) do not reach not equilibrium instantly. This has been observed both in experimental studies of thermal diffusion in aqueous solutions (e.g. Leist and Lv, 1990) and in numerical simulations in soil (e.g. [Thomas et al., 2012 ; Xie et al., 2015c]). thus, the variation of temperature in the clay liners with time should be considered .

Thermal diffusion coefficient of a single chemical species is described by (Yan et al., 2020)

$$D_T = D(T) S_T C \quad (14)$$

Substituting Eq. (14) into Eq. (13), The heat transfer in unsaturated CCL under unsteady-state can be presented as

$$\frac{\partial T}{\partial t} = D_0 S_T \frac{\partial}{\partial z} \left((MT + N) c \frac{\partial T}{\partial z} \right) \quad (15)$$

These coupled equations (equations 12 and 15) are partial differential equations (PDE) with variable coefficients. It is generally impossible to obtain an analytical solution in closed form under these conditions. This observation forces us to think about the digital approach in the remainder of this work.

For a heterogeneous semi-infinite domain in which the initial concentration is

$$C(z, 0) = C_i , \quad (16)$$

and the chemical concentration on the surface is constant, i.e.

$$C(0, t) = C_0, \quad (17)$$

with the other boundary assumed to be impermeable, i.e.,

$$\frac{\partial C(L,t)}{\partial z} = 0 \quad (18)$$

The model also incorporated seasonal temperature variations at the ground surface to realistically predict the temporal distributions of temperature within the landfills. The seasonal temperature variations were applied at the ground surface and were represented by a sinusoidal function using Eq. (19) (Hanson et al., 2022)

$$T(0, t) = T_m + A_s \cos \left[\frac{2\pi}{\tau_0} (t - t_0) \right] \quad (19)$$

where $T(0, t)$ = surface temperature at a specific time ($^{\circ}\text{C}$); T_m = mean surface temperature ($^{\circ}\text{C}$); A_s = amplitude of the temperature wave ($^{\circ}\text{C}$); τ_0 = is the period of the thermal wave (365 days) ; t = time (s); and t_0 = phase constant used to correctly represent the Julian calendar and is equal to 3,939,840 s (i.e., 45.6 days). The lower boundary temperature is usually considered as constant temperature.

3. Techniques of computation: implementation of the MATLAB pdepe solver

MATLAB's pdepe solver is a function that solves initial-boundary value problems for systems of partial differential equations (PDEs). It is specifically designed for solving time-dependent PDEs with one spatial variable. This solver converts the PDEs to ODEs using a second-order accurate spatial discretization based on a set of nodes specified by the user. The discretization method is described in (Skeel & Berzins, 1990). It discretizes the spatial domain using a finite difference method and then applies an ODE solver to solve the resulting system of ordinary differential equations (ODEs). The time integration is done with ode15s. The main advantage of pdepe solver is its ease of use. It requires users to provide the system of PDEs, initial conditions, boundary conditions, and other parameters. Additionally, it allows users to specify the problem as a set of coefficient form PDEs or as a set of equations with specified functional forms. Overall, MATLAB's pdepe solver is a powerful tool for solving time-dependent PDE problems with one spatial variable. It is widely used in various scientific, engineering, and mathematical fields to solve a wide range of real-world problems.

To demonstrate the concentration distributions of an input source of uniform nature, the numerical solutions of the governing equation (1) are displayed graphically using the given input parameters. In this case, the coating is assumed to be finite and heterogeneous, and the variation of the concentration in space and time is examined. The numerical solutions are obtained using the MATLAB pdepe solver and the concentration behavior is displayed graphically. The common input data taken in this article are chosen from previously published literature or empirical relationships (Jiang et al., 2023; Yan et al., 2020). The Neumann-type lower limit is adopted.

4. Results and discussion

4.1. Validation of the numerical approach for soil solute transport

For numerical illustration, a solute transport of a 3 m initially dry semi-infinite porous media depth is considered. In this domain the diffusion of a non-reactive chemical species in water, under a thermal and chemical gradient is studied. The effect of temperature on chemical diffusion coefficient is neglected in this test. A constant diffusivity is employed as $D_0 = 10^{-9} \text{ m}^2/\text{s}$. The source or sink quantities are neglected. The inlet chemical concentration is

set at 100mol/m^3 , whilst the outlet and initial chemical concentrations are $0,01\text{mol/m}^3$. The Neuman condition is applied to the output. The other physical parameters used are: i) the Soret coefficient $S_T = 0.01 \text{ }^\circ\text{K}^{-1}$, ii) temperature at inlet boundary is assumed to be constant ($333 \text{ }^\circ\text{K}$) and temperature at outlet boundary is assumed to be fixed at $295 \text{ }^\circ\text{K}$. Heat transfer is assumed to be under steady state. Therefore, the heat profile can be obtained through eq(20).

$$T = 333 - 4z \tag{20}$$

The analytical solution of equation (10) can be obtained using a Laplace transformation technique (Yadav et., 2023). For a porous medium depth L with the initial and boundary conditions described by Eqs. (16), (17) and (18) we have:

$$\begin{aligned} \frac{c(z,t)-c_i}{c_0-c_i} = & \frac{1}{2} \operatorname{erfc} \left(\frac{z+GD_0S_Tt}{2\sqrt{Dt}} \right) + \frac{1}{2} \exp \left(\frac{-GD_0S_Tz}{D} \right) \operatorname{erfc} \left[\frac{-GD_0S_Tt+z}{2\sqrt{Dt}} \right] + \\ & \frac{1}{2} \left[2 - \frac{GD_0S_T(2L-x)}{D} + \frac{(GD_0S_T)^2t}{D} \right] \exp \left(-\frac{GD_0S_TL}{D} \right) \operatorname{erfc} \left(\frac{2L-z-GD_0S_Tt}{2\sqrt{Dt}} \right) - \\ & \sqrt{\frac{(GD_0S_T)^2t}{\pi D}} \exp \left(-\frac{GD_0S_TL}{D} - \frac{(2L-z-GD_0S_Tt)^2}{4Dt} \right) \end{aligned} \tag{21}$$

where erfc denotes the complementary error function.

Figure 2 gives a comparison of the MATLAB pdepe solver solutions of the diffusion equation with the analytical results. The effects of the variable depth of the medium (fig.2a) and the propagation of the relative error with depth (fig.2b) are also represented. Figure 3 represents the temporal evolution of the solute for three different depths. Excellent agreement is obtained between the numerical results and the analytical predictions. In each soil depth, the result obtained with the MATLAB pdepe solver precisely matches the analytical value with a maximum relative error between solutions less than 3%. These results presented in Figure 2.b show that the proposed numerical scheme is precise and effective in predicting the transport phenomenon in a composite coating.

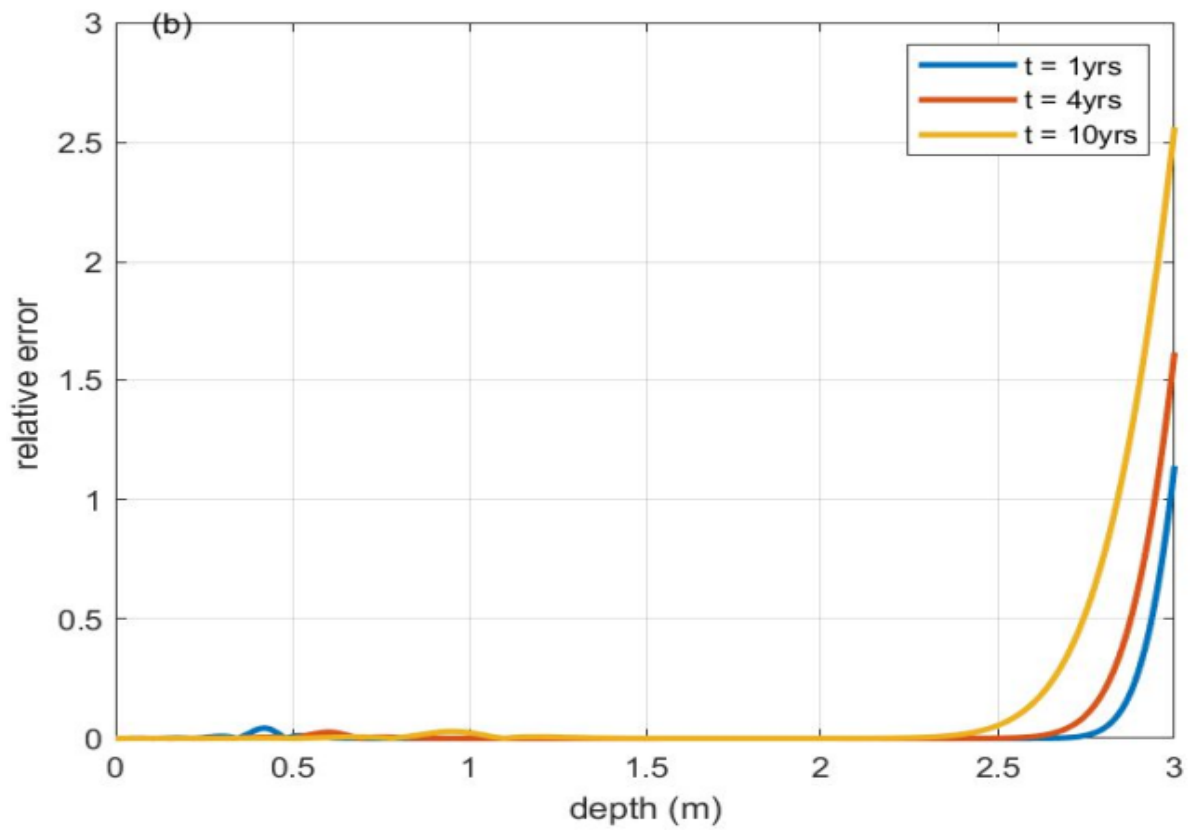


Fig.2. Comparison of numerical and analytical results for concentration versus distance (a) and Propagation of the relative error (b)

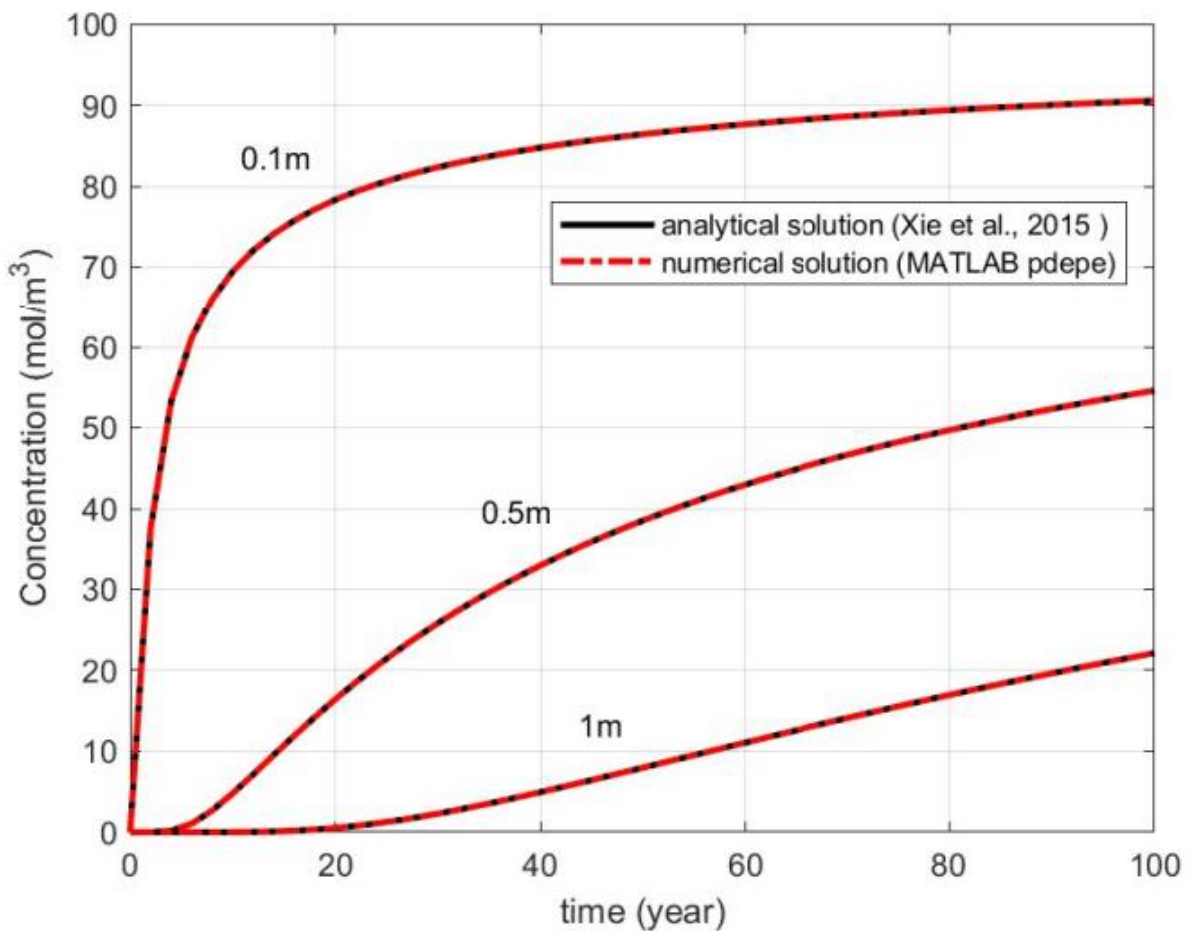


Fig.3. Comparison of numerical and analytical results for concentration versus time

4.2. Model application for coupled thermal and chemical diffusion in porous media

In this section, thermally induced diffusion of chemicals in saturated porous media will be studied. The main objective is to study the extent of the effects of primary governance processes and parameters in unsteady regimes. Comparisons of numerical results of predictions of environmental solutes obtained in steady and transient states are illustrated for spatial variations. The interest is in particular to obtain an evaluation of the temporal variation of the temperature over the entire process. The effects of two key parameters, including the temporal variation of temperature and the Soret coefficient (S_T) on chemical diffusion, are analyzed. In order to evaluate the influence of temperature on chemical transport through the porous medium, four simulation cases (scenarios) were designed:

Case 1 which consists of studying the problem under molecular diffusion only and diffusion coefficient variable with temperature (i.e. DT) in permanent heat transfer regime,

Case 2 which consists of studying the problem under molecular diffusion only and diffusion coefficient variable with temperature (i.e. DT) in unsteady heat transfer regime ,

Case 3 which combines molecular diffusion, Soret effect and diffusion coefficient variable with temperature for heat transfer in steady state (Yan et al., 2020),

and

Case 4 for which the combined effects of molecular diffusion, Soret effect, variable diffusion coefficient (DT) and transient regime of heat transfer are considered.

Comparisons between cases 1 and 2, cases 3 and 4 can provide evidence of the influence of the transient state of heat transfer. The comparison between case 1 and case 3 can highlight the influence of the soret effect in steady state. A comparison between cases 2 and 4 can reveal the relative importance of the effect of the soret effect in the unsteady heat transfer regime.

A saturated porous medium of one unit length (3 m) is considered in this section. The initial chemical concentration (hypothetical species) in the domain is assumed to be equal to $0.01 \text{ mol}/\text{m}^3$. The input chemical concentration is set at $C_0 = 100 \text{ mol}/\text{m}^3$. At the output limit the Neumann boundary condition is considered ($\partial C/\partial x = 0$). The Soret coefficient and porosity are 0.01°K^{-1} and 0.5, respectively. The average temperature and the temperature amplitude at the inlet boundary are assumed to be 333°K and 15°K respectively. The temperature at the outlet limit is assumed to be fixed at 295°K . The diffusion coefficient is considered to be $10^{-10} \text{ m}^2/\text{s}$ at the ambient temperature of 295°K . The variation of the diffusion coefficient with temperature is calculated using Eq. 10.

Figure 9 presents a comparison between the chemical concentration profile at 50 years for the four cases cited above. Significant differences can be found for the chemical concentration profile between these four cases.

As shown in Figure 9, the concentration of the chemical at $x = 1.2 \text{ m}$ (arbitrary location in the domain and at 50 years) for simulation cases 1 and 3 is $11.28 \text{ mol}/\text{m}^3$ and $12.19 \text{ mol}/\text{m}^3$ respectively. These values are 2.05 and 1.56 times higher than that calculated respectively

for cases 2 and 4. These cases demonstrate the importance of thermally coupled processes in the transient regime in the diffusion problem.

The results of the presented simulation series demonstrate that the chemical mass flux is increased by thermal diffusion. This increase is greater in the transitional regime. This is evident from the chemical concentrations calculated for case 4, which are considerably higher than those for the diffusion scenario without Soret effect (case 2). The results show that the chemical concentration for case 4 is 1.42 times higher than that of case 2 (see Fig. 4). However, the results show that in steady state, the Soret effect does not have a considerable influence on the rate of chemical transport in the field. This is similar to the conclusion obtained by Yan et al. in 2020 (Yan et al., 2020). Yan et al. [28] showed that without taking into account the Soret effect, variations in DT with temperature alone can significantly increase the rate of chemical transport in the domain. The results show that the chemical concentration for case 3 is 1.08 times higher than that of case 1 (see Fig. 4). In summary, the results presented in Fig (4) show that heat transfer in unsteady regime can considerably affect chemical diffusion through porous media in particular by the Soret effect and by the temperature dependence of chemical diffusion (DT). This is best illustrated in the following figure 4. Figure (5a) illustrates the spatial variation of the solute concentration for four simulation times $t = \{2, 10, 30, 50\}$ years for the cases of heat transfer in steady and unsteady regimes, while the spatial distribution of the difference between the two simulated regimes is given in figure (5b). Figure (5c) presents the temporal variation at soil depths $z = \{0.1, 0.5, 0.7, 1\}$ m, while Figure (5d) depicts the corresponding absolute error.

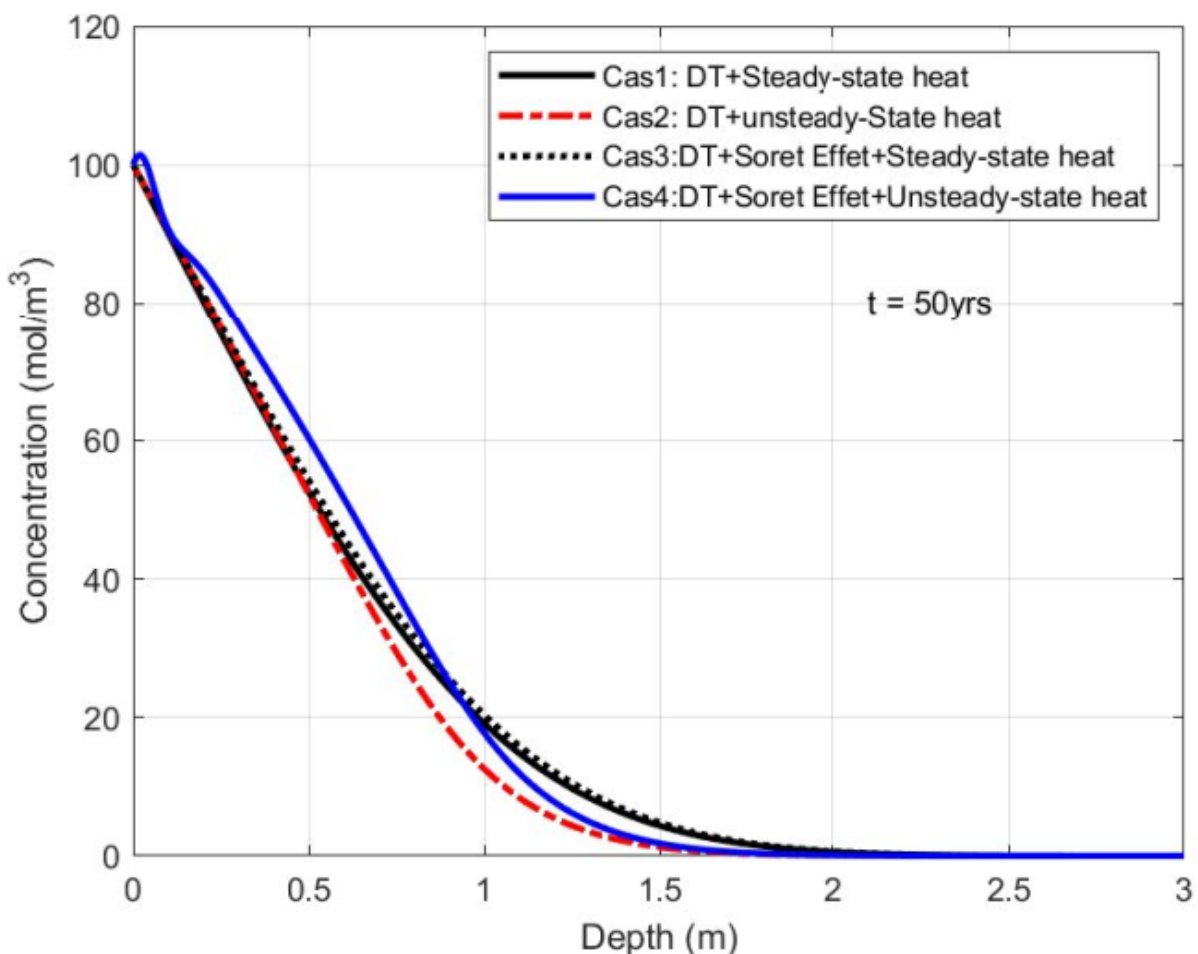


Fig.4. Variations of concentration with depth for different simulation cases

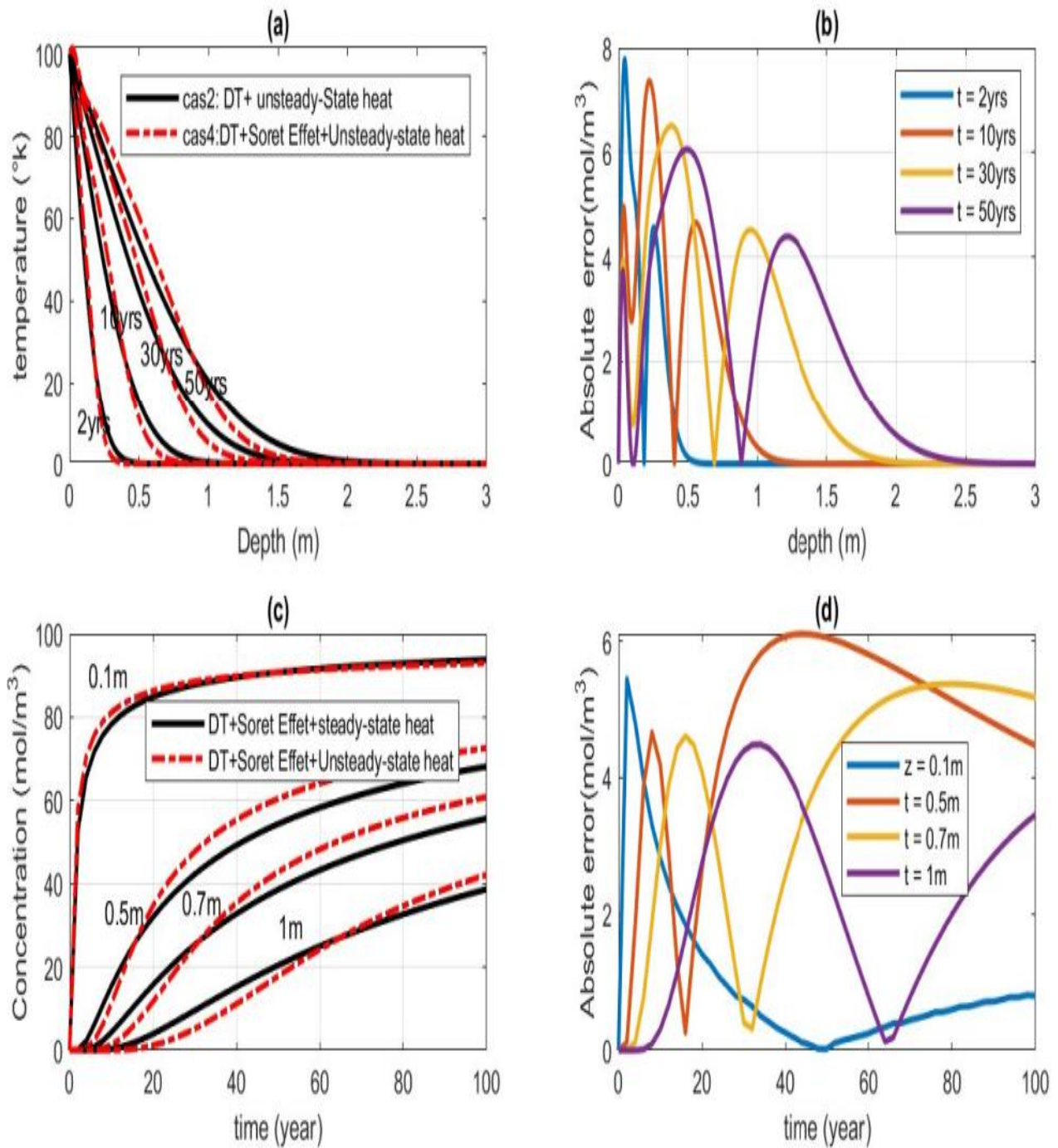


Fig. 5. Distribution of solute concentration for different simulation times and for different media depths in the case of an average temperature of 333°K at the upper surface of the media

4.3. Influence of variable average ambient temperature on unsaturated soil solute distribution

Figure (6) illustrates the temporal profiles of solute concentration for depths of $z = \{0.5; 1.2\}$ m. These results are obtained for three different temperatures, namely 323, 353 and 373 on the surface of the clay coating. The Soret coefficient and the surface concentration are here assumed to be $0.01^{\circ}K^{-1}$ and $100 \text{ mol}/m^3$ respectively. The solute concentration distribution curves with steady-state and unsteady heat transfer for different temperatures are shown in Figure 7a and b, respectively. The transport of solutes in the material at both depths shows a

similar variation for the two regimes, even when increasing the temperature change at the upper surface. It is indicated that the concentration at a given depth increases with increasing average temperature at the surface of the clay coating. This increase is greater when the heat transfer is taken in an unsteady state. For example, the concentration at a depth of 0.5m at the 40-year date is 45.58 mol/m^3 and 60.67 mol/m^3 for the case of thermal diffusion in steady state respectively with $T_m = 323 \text{ }^\circ\text{K}$ and $T_m = 373 \text{ }^\circ\text{K}$. The overestimation rate of breakthrough concentration is 33.10%.

However in unsteady regime, at the same position and on the same date, the concentration of 49.74 mol/m^3 and 73.86 mol/m^3 with $T_m = 323 \text{ }^\circ\text{K}$ and $T_m = 373 \text{ }^\circ\text{K}$, respectively. The overestimation rate of breakthrough concentration is 48.49%. These results show that the temperature acting on the surface of the clay coating has a great influence on the penetration of contaminants through the coating. The effect of thermal diffusion and temporal temperature variation must be taken into account when designing clay landfill linings. Due to thermal coupling, the solute transport response under unsteady state heat transfer conditions is then associated with the temperature gradient as well as the temporal variation of the temperature. these are not taken into account in most modeling approaches (Peng et al., 2023; Yan et al., 2020). (Peng et al., 2023; Yan et al., 2020).

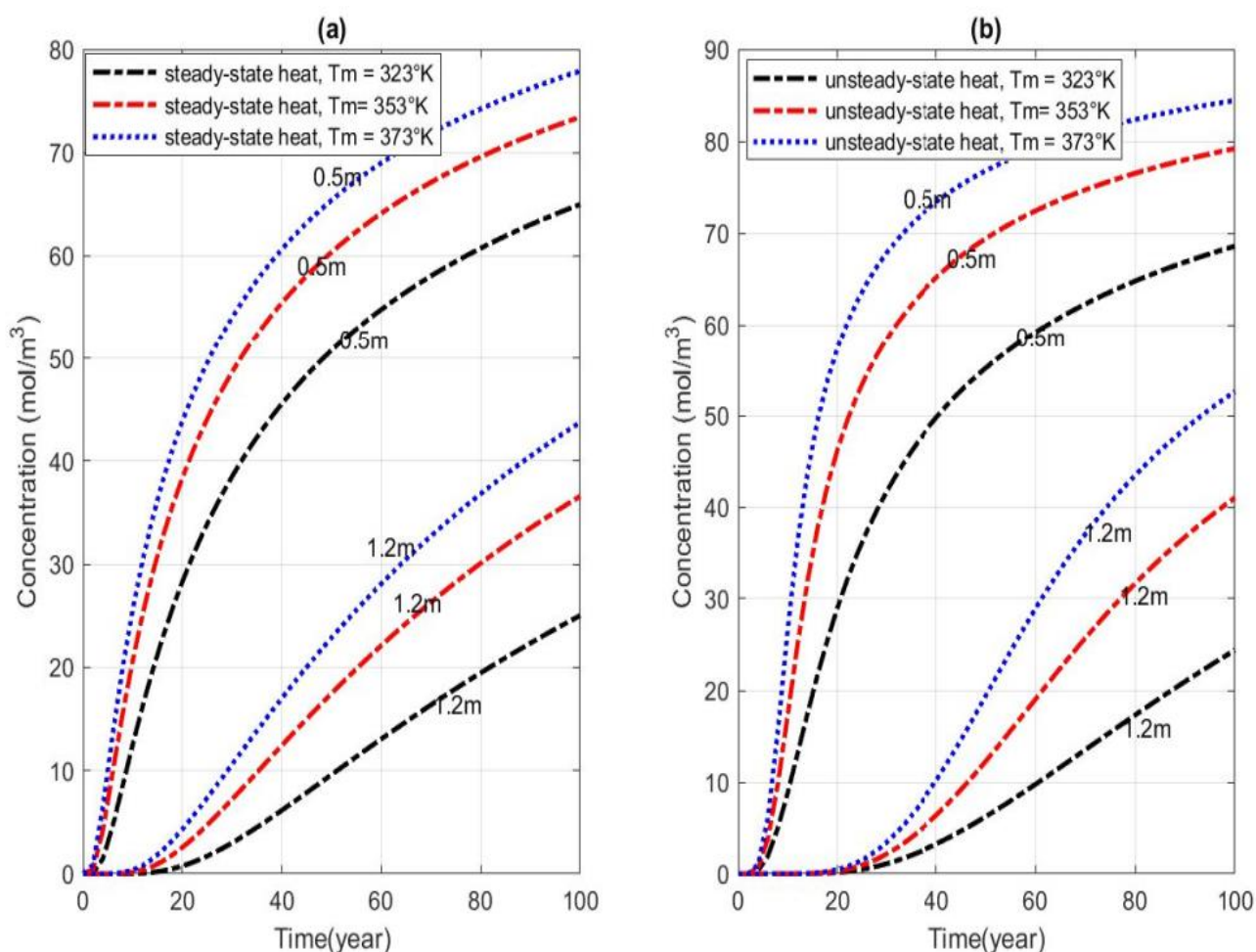


Fig. 6. Solute breakthrough profiles for different transport responses in soil depths $z = \{0.5; 1.2\}m$

4.4. Effects of concentration on temperature

Figure (7) shows the variation of the temperature profiles with time at two different depths $z = \{2, 5\}$ cm, for three values of the initial concentration at the surface of the coating $C_0 = \{100, 500, 1000\} \text{ mol/m}^3$. The simulations were repeated considering an average temperature of $333 \text{ }^\circ\text{K}$ at the surface and an ambient temperature of $295 \text{ }^\circ\text{K}$ within the medium. Using these values in the simulations, results closer to the unsteady analysis with a variable diffusion coefficient are obtained. We see that the temperatures calculated at a given depth are quite close at the beginning. Subsequently, These results show that the temperature evolves quickly to reach a relatively stable state. In this phase, it is indicated that the temperature propagation is relatively rapid at a relatively high initial surface concentration. For example, for a depth of 0.5 m , the temperature remains constant after 4 years and is equal to ambient temperature (295°K) for the different initial concentrations. however for the same depth, the temperatures after 20 years are 300.49°K , 319.18°K and 324.74°K for the initial concentrations 100 mol/m^3 , 500 mol/m^3 and 1000 mol/m^3 respectively. The result of figure (7) shows that the decrease in concentration also causes a significant delay in the temporal evolution of the temperature. for a depth of 1.2m , we witness a temporal variation in temperature after 60 years, 32 years and 22 years respectively for the three concentrations $C_0 = \{100, 500, 1000\} \text{ mol/m}^3$. It should be noted that the impact of transient heat flow conditions is neglected in several works relating to the diffusion of chemicals in a porous medium. And yet this condition has a significant impact on the results, especially when the initial concentrations at the surface are high.

© GSJ

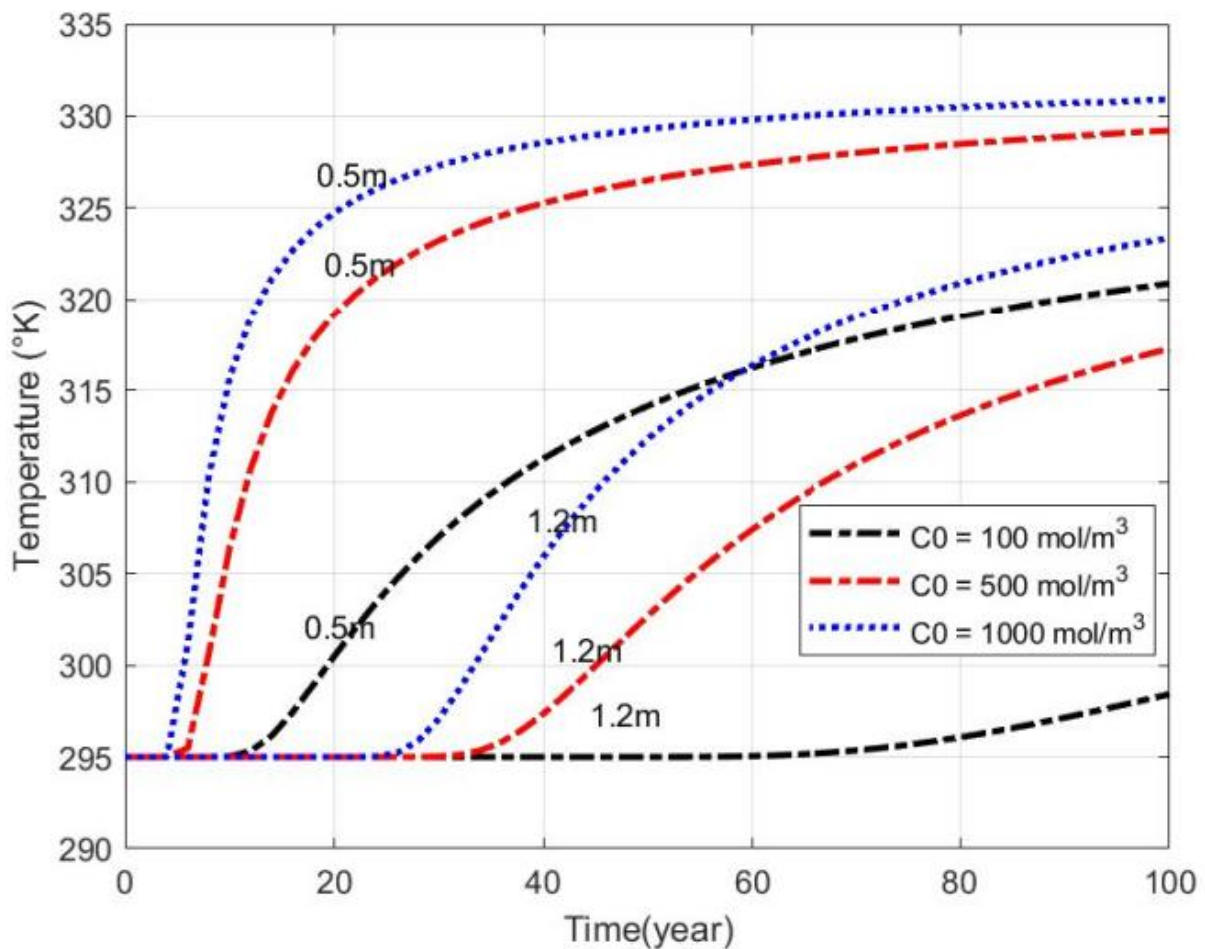


Fig.7. Temporal temperature profiles for different initial concentrations at the surface in the depths of the media $z = \{0.5; 1.2\}m$

5. Conclusion

In this paper, the effects of molecular diffusion and thermal diffusion on mass transfer in compacted clay coatings are studied numerically. The prediction of the solute profile in the environment, from the surface to the bottom, was examined. The heat and mass transport process studied was described by one-dimensional coupled partial differential equations. The analysis was carried out with varying diffusion coefficients. Two cases of solute diffusion combined with the Soret effect were analyzed: solute diffusion under stationary heat transfer conditions and solute diffusion under unsteady heat transfer conditions. The MATLAB pdepe solver was adopted to solve the equations governing heat and mass transfer processes and good numerical predictions were obtained. The effects of the thermal factor as well as their importance in capturing the spatio-temporal profile of solutes were examined. The analysis presented shows that the Soret effect significantly influences solute transport in unsteady regime. Compared to this regime, solute transfer responses with stationary thermal transfer suggest that the solute present in a subspace can be underestimated or overestimated as a function of time. It was also found that a temporal variation in the temperature of the medium affects the migration of solutes in the medium. For example, for an initial concentration of the solute at the surface $C_0 = 100 \text{ mol/m}^3$, the concentration gap between the two regimes can go up to 8 mol/m^3 . Similarly, an increase in average soil temperature induces rapid movement

of solute in the domain. The overestimation rate of breakthrough concentration when going from 323°K to 373°K is 48.49%. From the present numerical study, we observed that the temperature profiles increase with the increase in the initial concentration at the surface. Solute transport based on unstable thermal considerations produces more precise responses than movement configured in a stationary heat transfer regime. Research into these processes allows for a quantitative assessment of the contaminant transport processes necessary to design an efficient and well-operational coating system.

References

- Chao, K.P., Wang, P., Wang, Y.T., 2007. Diffusion and solubility coefficients determined by permeation and immersion experiments for organic solvents in HDPE geomembrane. *J. Hazard. Mater.* 132 (5), 519–526.
- Chen, R., Ge, Y., Chen, Z., Liu, J., Zhao, Y., Li, Z., 2019. Analytical solution for onedimensional contaminant diffusion through unsaturated soils beneath geomembrane. *J. Hydrol.* 568, 260–274.
- Chen, Y., Wang, Y., Xie, H., 2015. Breakthrough time-based design of landfill composite liners. *Geotext. Geomembr.* 43 (2), 196–206.
- Edil, T.B., 2003. A review of aqueous-phase VOC transport in modern landfill liners. *Waste Manage.* 23, 561–571.
- Engelhardt, G.R., Lvov, S.N., Macdonald, D.D., 1997. Importance of thermal diffusion in high temperature electrochemical cells. *J. Electroanal. Chem.* 429 (1–2), 193–201.
- Feng, S.J., Peng, M.Q., Chen, Z.L., Chen, H.X., 2019a. Transient analytical solution for one-dimensional transport of organic contaminants through GM/GCL/SL composite liner. *Sci. Total Environ.* 650, 479–492.
- Feng, S.J., Peng, M.Q., Chen, H.X., Chen, Z.L., 2019b. Fully transient analytical solution for degradable organic contaminant transport through GMB/GCL/AL composite liners. *Geotext. Geomembr.* 47, 282–294
- Guan, C., Xie, H.J., Wang, Y.Z., Chen, Y.M., Jiang, Y.S., Tang, X.W., 2014. An analytical model for solute transport through a GCL-based two-layered liner considering biodegradation. *Sci. Total Environ.* 466, 221–231.
- Harris, K. R., & Woolf, L. A. (1980). Pressure and temperature dependence of the self diffusion coefficient of water and oxygen-18 water. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 76, 377-385.
- Leaist, D.G., Lv, H., 1990. Conductometric determination of the Soret coefficients of a ternary mixed electrolyte, reversed thermal diffusion of sodium chloride in aqueous sodium hydroxide solutions. *J. Phys. Chem.* 94, 447–451.
- Liu, C., Ball, W.P., 1998. Analytical modeling of diffusion-limited contamination and decontamination in a two-layer porous medium. *Adv. Water Resour.* 21 (4), 297–313.

- Liu, G., Barbour, L., Si, B.C., 2009. Unified multilayer diffusion model and application to diffusion experiment in porous media by method of chambers. *Environ. Sci. Technol.* 43 (7), 2412–2416.
- Lu, S.F., Feng, S.J., 2022. Coupled bio-hydro-thermo-mechanical interactions of landfilled MSW based on a multi-phase, multi-component numerical model. *Comput. Geotech.* 144, 104659.
- Lu, S.F., Feng, S.J., Zheng, Q.T., Bai, Z.B., 2021. A multi-phase, multi-component model for coupled processes in anaerobic landfills: Theory, implementation, and validation. *Geotechnique* 71, 826–842.
- Mohanty, R. R.; Guyer, J. E.; and Sohn, Y. H., 2009. Diffusion under temperature gradient: A phase-field model study . Faculty Bibliography 2000s. 1917.
- Mon, E. E., Hamamoto, S., Kawamoto, K., Komatsu, T., & Moldrup, P. (2016). Temperature effects on solute diffusion and adsorption in differently compacted kaolin clay. *Environmental Earth Sciences*, 75, 1-9.
- Peng, M.Q., Feng, S.J., Chen, H.X., Chen, Z.L., Xie, H.J., 2020. Analytical model for organic contaminant transport through GMB/CCL composite liner with finite thickness considering adsorption, diffusion and thermodiffusion. *Waste Manag.* 120, 448–458.
- Peng, M. Q., Feng, S. J., Chen, H. X., & Chen, Z. L. (2021). An analytical solution for organic pollutant diffusion in a triple-layer composite liner considering the coupling influence of thermal diffusion. *Computers and Geotechnics*, 137, 104283.
- Peng, M. Q., Feng, S. J., Chen, H. X., & Chen, Z. L. (2023). The role of thermodiffusion in organic pollutant transport in landfill composite liner system. *Computers and Geotechnics*, 153, 105108.
- Pu, H., Qiu, J., Zhang, R., Zheng, J., 2020. Analytical solutions for organic contaminant diffusion in triple-layer composite liner system considering the effect of degradation. *Acta Geotech.* 15 (4), 907–921.
- Qiu, J., Pu, H., Chen, X., Zheng, J., 2021. Analytical solutions for contaminant diffusion in four-layer sediment-cap system for subaqueous in-situ capping. *Geotext. Geomembr.* 49 (2), 376–387.
- Rahman, M.A., Saghir, M.Z., 2014. Thermodiffusion or Soret effect: Historical review. *Int. J. Heat Mass Tran.* 73, 693–705.
- Rosanne, R., Paszkuta, M., Tevissen, E., & Adler, P. M. (2003). Thermodiffusion in compact clays. *Journal of Colloid and Interface Science*, 267(1), 194-203.
- Rowe, R.K., Jones, D., Rutter, A., 2016. Polychlorinated biphenyl diffusion through HDPE geomembrane. *Geosynth. Int.* 23 (6), 408–421.
- Shackelford, C.D., 2014. The ISSMGE Kerry Rowe Lecture: the role of diffusion in environmental geotechnics. *Can. Geotech. J.* 51, 1219–1242.
- Skeel, R. D., & Berzins, M. (1990). A method for the spatial discretization of parabolic equations in one space variable. *SIAM journal on scientific and statistical computing*, 11(1), 1-32.

Thomas, H.R., Sedighi, M., Vardon, P.J., 2012. Diffusive reactive transport of multicomponent chemicals under coupled thermal, hydraulic, chemical and mechanical conditions. *Geotech. Geol. Eng.* 30 (4), 841–857.

Wu, X., Shi, J., 2017. Analytical solutions for diffusion of organic contaminant through composite liner considering degradation in leachate and soil liner. *Int.J. Environ. Pollut.* 61 (2), 166–185.

Xie, H., Chen, Y., Lou, Z., 2010. An analytical solution to contaminant transport through composite liners with geomembrane defects. *Sci. China. Technol. Sci.* 53 (5), 1424e1433.

Xie, H., Lou, Z., Chen, Y., Jin, A., Chen, P., 2011. An analytical solution to contaminant advection and dispersion through a GCL/AL liner system. *Chin. Sci. Bull.* 56 (8), 811–818.

Xie, H., Jiang, Y., Zhang, C., Feng, S., 2015a. An analytical model for volatile organic compound transport through a composite liner consisting of a geomembrane, a GCL, and a soil liner. *Environ. Sci. Pollut. Res.* 22 (4), 2824–2836.

Xie, H., Thomas, H.R., Chen, Y., Sedighi, M., Zhan, T.L., Tang, X., 2015b. Diffusion of organic contaminants in triple-layer composite liners: an analytical modeling approach. *Acta Geotech.* 10 (2), 255–262.

Xie, H., Zhang, C., Sedighi, M., Thomas, H.R., Chen, Y., 2015c. An analytical model for diffusion of chemicals under thermal effects in semi-infinite porous media. *Comput. Geotech.* 69, 329–337

Xie, H., Zhang, C., Feng, S., Wang, Q., Yan, H., 2018. Analytical model for degradable organic contaminant transport through a GMB/GCL/AL system. *J. Environ. Eng.* 144 (3), 04018006.

Yu, C., Wang, H., Fang, D., Ma, J., Cai, X., Yu, X., 2018. Semi-analytical solution to onedimensional advective-dispersive-reactive transport equation using homotopy analysis method. *J. Hydrol.* 565, 422–428.

Yadav, R. R., Kumar, L. K., & Kushwaha, S. (2023). Numerical solution of non-linear advection-dispersion equation in a finite porous domain. *International Journal of Engineering, Science and Technology*, 15(3), 32-42.

Yan, H., Sedighi, M., & Xie, H. (2020). Thermally induced diffusion of chemicals under steady-state heat transfer in saturated porous media. *International Journal of Heat and Mass Transfer*, 153, 119664.

Yan, X., Duan, Z., Sun, Q., 2021. Influences of water and salt contents on the thermal conductivity of loess. *Environ. Earth Sci.* 80 (2), 1–14.

Zhan, L.T., Zeng, X., Li, Y., Chen, Y., 2013. Analytical solution for one-dimensional diffusion of organic pollutants in a geomembrane-bentonite composite barrier and parametric analyses. *J. Environ. Eng.* 140 (1), 57–68.