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through soil barriers**

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The role of diffusion in contaminant migration through soil barriers

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ABSTRACT. This paper describes the role of diffusion in governing the transport of contaminants through soil (mineral) barriers (e.g., soil liners and slurry walls). The specific topics covered include the significance of diffusive transport through porous media, the relative significance of the various parameters affecting contaminant migration, and the effects of various modelling assumptions for the design of soil barriers.

Charts for preliminary design utilizing dimensionless parameters are presented for the purpose of illustrating the role of diffusive transport through soil barriers for both transient and steady-state conditions for three different waste containment scenarios: (1) pure diffusion, (2) diffusion and advection in the same direction, and (3) diffusion against advection.

The design charts allow for analyses to determine the basic features of a barrier referring to either contaminant concentration or contaminant mass flux. The analyses show that a low hydraulic conductivity for the soil is a necessary, but not sufficient, condition for the design of a successful barrier. Failure to recognize the role of diffusion in barrier design can lead to extremely unconservative designs. The assumption of steady-state seepage flow of the solvent (water) and the boundary conditions employed in the analysis methods are shown to be approximations for actual field conditions, but are useful in terms of providing simplified assessments of barrier performance.

Emphasis is placed on conservative assumptions when the proposed analytical models are used. A laboratory method for measuring effective diffusion coefficients and the application of measured values for design of soil barriers also are illustrated.

1. Introduction

Over the past decade or so, numerous studies have indicated that diffusion may be a significant, if not dominant, transport process in fine-grained soils used for waste containment barriers [e.g., GOODALL and QUIGLEY, 1977; DESAULNIERS *et al.*, 1982, 1986; CROOKS and QUIGLEY 1984; QUIGLEY and ROWE, 1986; QUIGLEY *et al.*, 1987; JOHNSON *et al.*, 1989]. Based on this evidence, it appears that a low hydraulic conductivity is a necessary, but not sufficient, condition to assure adequate performance of soil barriers (e.g., compacted clay liners or slurry walls).

The purpose of this paper is to describe the role of diffusion in governing the migration of contaminants through soil barriers used for waste containment. Analyses are presented for simplified boundary conditions associated with waste containment scenarios to illustrate the influence and significance of diffusive transport.

2. Transport processes

In the absence of coupled flow processes (e.g., osmosis), the migration of contaminants in homogeneous, saturated soil is governed by three transport processes, viz., advection, diffusion, and dispersion. Mass flux of solute (contaminant) due to advection, J_a , is given by:

$$J_a = qc = nvc = (-K \nabla h) c \quad (1)$$

where q is the Darcian or fluid flux, c is the solute

concentration in the pore liquid, n is the soil (barrier) porosity, v is the average linear or seepage velocity, K is the hydraulic conductivity (permeability) of the soil (barrier), and ∇h is the gradient in total head, h . The diffusive mass flux is given by Fick's first law, or:

$$J^* = -nD^* \nabla c \quad (2)$$

where ∇c is the concentration gradient and D^* is the effective diffusion coefficient for diffusion in soil, or:

$$D^* = \tau D_o \quad (3)$$

In Eq. (3), τ is the apparent tortuosity factor (< 1) to account primarily for the tortuous nature of the migration pathways in soil and D_o is the diffusion coefficient in aqueous or free solution [SHACKELFORD and DANIEL, 1991a]. Since $\tau < 1$, diffusive mass transport is slower in soil than in aqueous solution.

The dispersive flux (also known as mechanical dispersion), J_d , takes into account the spreading of the solute due to the differences in the flow velocity in the single pore channels with respect to the average direction and magnitude of the seepage velocity in the porous medium (for more details see BEAR [1979]; FREEZE and CHERRY [1979]). The dispersive flux commonly is assumed to have the same form as Fick's first law for diffusion, or:

$$J_d = -nD \nabla c \quad (4)$$

where D is the (mechanical) dispersion coefficient.

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However, as already mentioned, the dispersive flux is attributed to variations in seepage velocity during migration, as opposed to variations in concentration. As a result, the dispersion coefficient usually is correlated with the seepage velocity as follows:

$$D = \alpha v \quad (5)$$

where α is the dispersivity of the porous medium. Based on Eqs. (4) and (5), dispersion increases as the seepage velocity, and vice versa. Therefore, at the low seepage velocities associated with flow through low permeability soil barriers, mechanical dispersion can be considered to be negligible [MITCHELL, 1992], and the total solute flux, J , can be taken as the sum of the advective and diffusive solute fluxes, or:

$$J = J_a + J^* = n(vc - D^* \nabla c) \quad (6)$$

For transient migration, the conservation of mass, (represented by the equation of continuity, FREEZE and CHERRY [1979]), states that:

$$nR \frac{\partial c}{\partial t} = -\nabla \cdot J \pm S \quad (7)$$

where S is a source/sink term and R is the retardation factor given by:

$$R = \frac{v}{v_c} \quad (8)$$

where v_c is the velocity of the center of mass of the contaminant [FREEZE and CHERRY, 1979; SHACKELFORD, 1993]. The retardation factor accounts for linear and reversible adsorption of solutes to the surfaces of soil particles and other soil or mineral constituents (e.g., organic matter, cement) during migration through the porous medium. For solutes subjected to adsorption, $R > 1$; otherwise, $R = 1$. As a result, the migration front for adsorbing contaminants lags the seepage front, whereas the migration front for non-adsorbing solutes is the same as the seepage front. In the absence of sources/sinks ($S=0$), the combination of Eqs. (6) and (7) results in an advection-diffusion equation for transient solute migration, or:

$$R \frac{\partial c}{\partial t} = D^* \nabla^2 c - v \nabla c \quad (9)$$

Solutions to Eq. (9) can be used to model advective-diffusive transport of miscible contaminants (solutes) through porous media. However, such models are limited by the assumptions inherent in the derivation of Eq. (9). Besides the assumptions that $D=S=0$ and linear reversible adsorption reactions, application of Eq. (9) implies a homogeneous, isotropic, and incompressible porous medium, steady-state seepage, and an incompressible fluid.

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3. Waste containment scenarios

With respect to waste containment by engineered soil barriers, three scenarios are important [SHACKELFORD, 1989; 1993]: (1) pure diffusion, (2) diffusion with positive advection, and (3) diffusion with negative advection. Each of these three scenarios is illustrated with respect to compacted clay liners and slurry walls in Fig. 1. The pure diffusion case results when there is no head difference across a soil barrier and, therefore, the advective flux is zero. However, due to the concentration gradient established across the soil barrier, contaminants still migrate from the containment side (c_0) to the external side ($c_1 < c_0$) of the barrier due to diffusion. This situation may result when a soil barrier is placed below the water table or when a slurry wall is placed around an existing contaminated area, e.g., for remediation.

The cases of diffusion with positive and negative advection result when a hydraulic gradient exists in the same or opposite direction, respectively, as the direction of the concentration gradient. Examples for the case of diffusion with positive advection are when the clay liner is placed above the water table or when the contaminated area, contained by the slurry wall, is not capped and infiltration (e.g., rainfall) accumulates in the containment area. Examples for the case of diffusion with negative advection are when a clay liner is placed below the water table, or over an artesian aquifer and when the groundwater table, within a contaminated area contained by a slurry wall, is lowered (e.g., by pumping) to induce inward advective flux [GRAY and WEBER, 1984; MANASSERO, 1991; MANASSERO and PASQUALINI, 1992]. Due to the nature of the problem, i.e., waste containment, diffusive flux conditions always exist. In the following analyses of the containment barrier systems, the internal pollutant concentration (upper boundary condition), c_0 , is always kept constant as a conservative assumption, whereas two different limit conditions are considered for the external pollutant concentration (lower boundary condition), c_1 , i.e.:

- transient conditions in which the concentration at an infinite distance from the barrier is zero (i.e., $c(x=\infty, t)=0$) and $c_1=f(t)$ at the outside end of the barrier, and
- steady-state mass flux conditions in which c_1 is

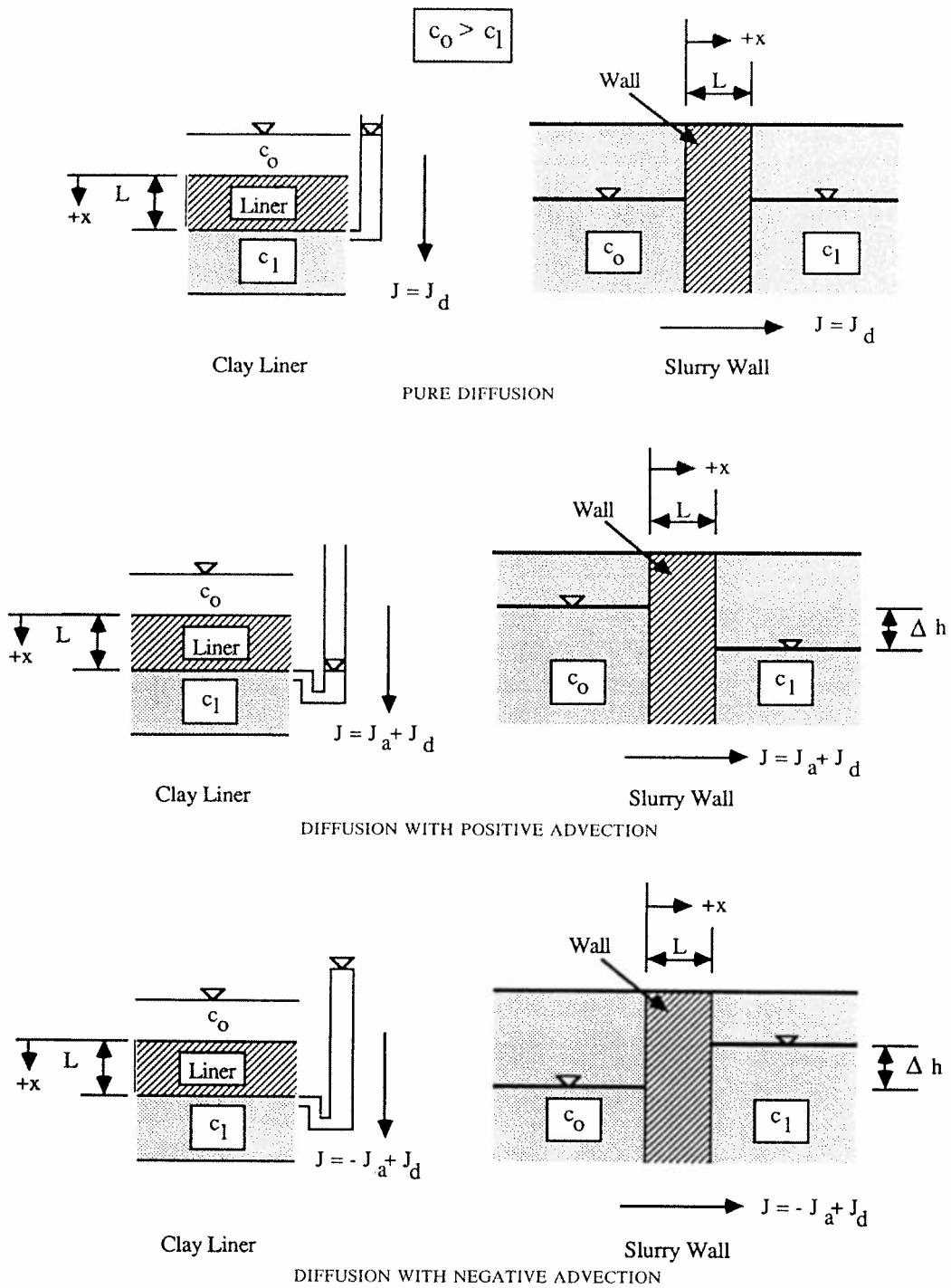


Fig. 1 - Waste containment scenarios for soil barriers [after SHACKELFORD, 1988; 1993].

Fig. 1 - Barriere per il contenimento di inquinanti; condizioni al contorno [da SHACKELFORD, 1988; 1993].

maintained constant at the outside end of the barrier.

4. Analytical models

For many practical situations, one-dimensional transport considerations are sufficient for describing the migration of contaminants through soil barriers used for waste containment. For one-dimensional transport in the x -direction, Eq. (9) becomes:

$$R \frac{\partial c}{\partial t} = D^* \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (10)$$

There are many analytical solutions to Eq. (10) depending on the initial and boundary conditions.

In the present case, the following initial and boundary conditions are assumed to apply for the general solution of the transient problem:

$$\left. \begin{aligned} c(x, t=0) &= 0 \\ c(x=0, t) &= c_0 \\ c(x=\infty, t) &= 0 \end{aligned} \right\} \quad (11)$$

Combination of Eqs. (10) and (11) results in the following analytical model for advective-diffusive transport [e.g., OGATA and BANKS, 1961; OGATA, 1970; BEAR, 1972; 1979; FREEZE and CHERRY, 1979; VAN GENUCHTEN and ALVES, 1984]:

$$\frac{c(x=L, t)}{c_0} = \frac{c_1}{c_0} = \frac{1}{2} \left\{ \operatorname{erfc} \left(\frac{RL - vt}{2\sqrt{D^* Rt}} \right) + \exp \left(\frac{vL}{D^*} \right) \operatorname{erfc} \left(\frac{RL + vt}{2\sqrt{D^* Rt}} \right) \right\} \quad (12)$$

where c_1/c_0 is the «relative concentration, RC», defined as the solute concentration at a distance, L , and time, t , relative to a constant inflow concentration, c_0 , and erfc is the complementary error function given by CARSLAW and JAEGER [1959], among others. For applications, it is convenient to write Eq. (12) in terms of dimensionless parameters as follows:

$$\frac{c_1}{c_0} = \frac{1}{2} \left\{ \operatorname{erfc} \left(\frac{1-T}{2\sqrt{T/P}} \right) + \exp(P) \operatorname{erfc} \left(\frac{1+T}{2\sqrt{T/P}} \right) \right\} \quad (13)$$

where T is the «advective time factor», and P is the Peclet number defined with respect to seepage

velocity, diffusion coefficient and the distance, L , or:

$$T = \frac{vt}{RL} = \frac{v_c t}{L}; \quad P = \frac{vL}{D^*} \quad (14)$$

The advective time factor, T , represents the pore volumes of solvent (water) flow for a column of length, L , divided by the retardation factor, R . Therefore, T equals the pore volumes of flow for a nonreactive solute ($R=1$), whereas the product RT equals the pore volumes of solvent flow for a reactive solute ($R>1$).

In the present study, Eqs. (12) or (13) are applied to describe transport only through a soil barrier of finite thickness, L . The upper boundary condition, assuming a constant source concentration, c_0 , is believed to be always conservative. The lower boundary condition, assuming a semi-infinite soil barrier, is not always appropriate; however, this assumption has been shown to result in relatively small errors (<5%) when Eqs. (12) or (13) are applied to describe miscible transport through finite laboratory columns [VAN GENUCHTEN and PARKER, 1984] and therefore, should be applicable to finite barriers under similar conditions.

In the case of steady-state concentration, Eq. (10) becomes:

$$D^* \frac{d^2 c}{dx^2} - v \frac{dc}{dx} = 0 \quad (15)$$

The general solution of Eq. (15) has the following form:

$$c = A + B \exp \left(\frac{vx}{D^*} \right) \quad (16)$$

where A and B are constants of integration.

As previously mentioned, the following boundary conditions are assumed to apply for steady-state conditions:

$$\left. \begin{aligned} c(x=0) &= c_0 = \text{constant} \\ c(x=L) &= c_1 = \text{constant} \end{aligned} \right\} \quad (17)$$

Combination of Eqs. (16) and (17) leads to the following closed-form solution for the general concentration, c , as a function of the distance in the barrier, x , or:

$$c = \frac{c_0 \exp(P) + (c_1 - c_0) \exp \left(\frac{vx}{D^*} \right) - c_1}{\exp(P) - 1} \quad (18)$$

Eq. (18) will be used in the following sections to describe long-term, steady-state conditions across the barrier scenario being considered.

5. Pure diffusion

For the case of pure diffusion, there is no seepage velocity (i.e., $v = 0$) and Eq. (10) reduces to Fick's second law for diffusion in soil, or:

$$R \frac{\partial c}{\partial t} = D^* \frac{\partial^2 c}{\partial x^2} \quad (19)$$

and the analytical model for pure diffusion results when $v=0$ is substituted into Eq. (12), or:

$$\frac{c_1}{c_0} = \text{erfc} \left(\frac{RL}{2\sqrt{D^*Rt}} \right) \quad (20)$$

The effective diffusion coefficients for most miscible contaminants in saturated soils range from $10^{-6} \text{ cm}^2/\text{s}$ ($0.003154 \text{ m}^2/\text{yr}$) to $10^{-5} \text{ cm}^2/\text{s}$ ($0.03154 \text{ m}^2/\text{yr}$), with a reasonable estimate for a nonreactive contaminant (e.g., Cl^-) of $5 \times 10^{-6} \text{ cm}^2/\text{s}$ ($0.01577 \text{ m}^2/\text{yr}$) [SHACKELFORD, 1991; SHACKELFORD and DANIEL, 1991 a]. Based on this value for D^* and on Eq. (20), relative solute concentrations, RC ($= c_1/c_0$) for the outflow end of a containment barrier have been plotted for a 100 yr period as a function of barrier thickness for nonreactive contaminants ($R=1$) in Fig. 2. Since the values for RC in Fig. 2 represent concentrations which may exceed allowable levels in many instances, diffusion through low-permeability barriers can be a significant transport process, especially for relatively thin barriers (i.e., $L \leq 1 \text{ m}$).

In order to evaluate the effect of pure diffusive transport for other values of D^* , R , and L , it is convenient to re-write Eq. (20) as follows:

$$\frac{c_1}{c_0} = \text{erfc} \left(\frac{1}{2\sqrt{T^*}} \right) \quad (21)$$

where T^* is a dimensionless «diffusive time factor», or:

$$T^* = \frac{D^*t}{RL^2} \quad (22)$$

Therefore, RC is related uniquely to T^* through Eq. (21), as shown in Fig. 3. Based on Eqs. (21) and (22), it is apparent that the time, t , required to reach a given value of RC and, therefore, T^* , will decrease as R and L decrease and/or D^* increases, with the effect of the barrier thickness (L) being the most significant factor.

In some instances, the solute flux, rather than the solute concentration, is a more pertinent parameter. The time-dependent diffusive solute flux can be evaluated by differentiating Eq. (12) with respect to « x », and substituting the result into Eq. (2) [SHACKELFORD, 1990], or:

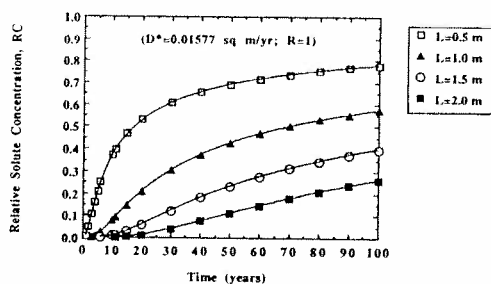


Fig. 2 - Effect of barrier thickness for breakthrough time versus relative concentration due to pure diffusive transport.

Fig. 2 - Influenza dello spessore della barriera sul tempo di attraversamento in funzione della concentrazione relativa nel caso di diffusione semplice.

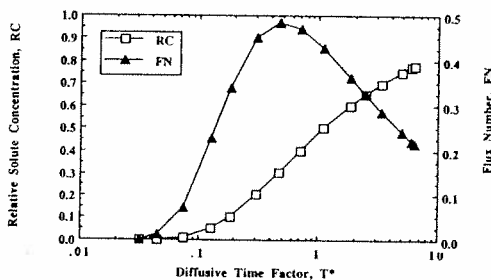


Fig. 3 - Diffusive time factor (Eq. 22) versus relative concentration ($= c_1/c_0$) and flux number (Eq. 25) for pure diffusive transport.

Fig. 3 - Fattore tempo diffusivo (Eq. 22) e numero di flusso (Eq. 25) in funzione della concentrazione relativa ($= c_1/c_0$) nel caso di diffusione semplice.

$$J^*(x=L, t) = \frac{1}{2} D^* n c_0 \left\{ \frac{2 \exp \left[- \left(\frac{RL - vt}{2\sqrt{D^*Rt}} \right)^2 \right]}{\sqrt{\pi \frac{D^*}{R} t}} - \frac{v}{D^*} \exp \left(\frac{vL}{D^*} \right) \text{erfc} \left(\frac{RL + vt}{2\sqrt{D^*Rt}} \right) \right\} \quad (23)$$

For the case of pure diffusion, v equals zero and Eq. (23) may be written in terms of dimensionless parameters as follows [SHACKELFORD, 1990]:

$$FN = \frac{\exp \left[- \left(\frac{1}{2\sqrt{T^*}} \right)^2 \right]}{\sqrt{\pi T^*}} \quad (24)$$

where FN is a dimensionless flux number defined as follows [SHACKELFORD, 1990]:

$$FN = \frac{J^*L}{nD^*c_0} \quad (25)$$

Based on Eqs. (24) and (25), the flux number also is related uniquely to the diffusive time factor, T^* . As a result, values of FN versus T^* also are plotted in Fig. 3.

Based on the plot of FN versus T^* in Fig. 3, FN increases to a maximum value of about 0.484 as T^* increases to a value of 0.498 and then FN decreases with increasing T^* values. This trend indicates that the diffusive solute flux increases until the concentration, at a distance L , begins to increase in a way such that the concentration gradient, $-\partial c/\partial x$, at $x=L$, begins to decrease. As equilibrium conditions are approached (i.e., as $t \rightarrow \infty$), $-\partial c/\partial x \rightarrow 0$ and the diffusive migration process stops.

If the concentration at the lower boundary, c_1 , is flushed continuously (e.g., by natural groundwater flow tangential to the external barrier surface), such that the outside barrier concentration is maintained at a constant value $c_1 < c_0$, then a steady-state condition eventually will result for the case of pure diffusion [SHACKELFORD, 1993].

Under steady-state diffusive flux conditions, a linear distribution of concentration results across the soil barrier, or:

$$c = c_0 + \left(\frac{c_1 - c_0}{L} \right) x \quad (26)$$

Eq. (26) results from placing $v=0$ (pure diffusion) in the general solution for steady-state conditions, Eq. (15), and performing the required integration. The steady-state diffusive flux under these conditions is given by:

$$J^* = -nD^* \left(\frac{c_1 - c_0}{L} \right) \quad (27)$$

In terms of flux number, the steady-state diffusive flux for this case is given by:

$$FN = 1 - \frac{c_1}{c_0} \quad (28)$$

or in the case of $c_1=0$, $FN=1$. Therefore, the steady-state mass flux, under the conditions where $c_1=0$, results in about double the maximum diffusive mass flux ($FN=0.484$) given by transient conditions assuming a semi-infinite barrier, all other conditions being equal.

6. Diffusion with positive advection

For the more common case of diffusion with positive advection (see Fig. 1), Eqs. (12) and (13) may be used directly to solve for the relative solute con-

centration, $RC (= c_1/c_0)$, at a distance L as a function of time. This procedure has been followed in terms of dimensionless parameters and the results for high and low Peclet numbers are plotted in Figs. 4a and 4b, respectively. Similar plots are provided by BEAR [1972; 1979]; and SHACKELFORD [1990; 1992]. As indicated in Fig. 4, diffusion becomes more significant relative to advection as the value of P decreases and breakthrough of the contaminant occurs sooner in terms of the advective time factor, T , for a given value of RC . This trend is further illustrated in Fig. 5 where P values versus T values have been plotted for relative solute concentrations, $RC (= c_1/c_0)$, of 0.01, 0.1, and 0.5. This trend previously has been noted elsewhere [BIGGAR and NIELSEN, 1961; DE WEIST, 1965; SHACKELFORD, 1988; 1992].

Based on the above trend, it might be concluded that diffusion-dominated transport results in earlier breakthrough of the contaminant than advection-dominated transport. However, this conclusion is valid only when the results are plotted in terms of dimensionless time, T . When the results are plotted in terms of real time, t , the reverse trend is apparent as shown in Fig. 6. The data for Fig. 6 are based on a barrier thickness of 1 m and D^* of $0.01577 \text{ m}^2/\text{yr}$ ($5 \times 10^{-6} \text{ cm}^2/\text{s}$).

The significance of the above trends is shown in Fig. 7 where the times required for a nonreactive ($R=1$) miscible contaminant to reach relative solute concentrations, RC , of 0.01, 0.1, and 0.5 at the effluent end of a 1-m thick soil barrier based on both pure diffusive transport and advective plus diffusive transport are plotted as a function of the seepage velocity, v . In addition, the transit times based on purely advective transport, i.e.,

$$t = \frac{L}{v_c} \quad (29)$$

where v_c is given by Eq. (8), also are plotted for comparison. In the case of pure advection (also commonly known as «piston» or «plug» flow), all of the contaminant reaches the distance L at the same time and, therefore, RC goes from a value of zero to a value of 1 «instantaneously». Based on the plots in Fig. 7, the advective plus diffusive transport times approach the times for pure diffusive transport as the seepage velocity decreases, as might be expected from intuition.

However, the transit times based solely on advective transport (Eq. 29) increase beyond those times predicted by pure diffusive transport as the seepage velocity decreases. Therefore, as the seepage velocity (or P) decreases, breakthrough of solutes under purely diffusive transport conditions requires

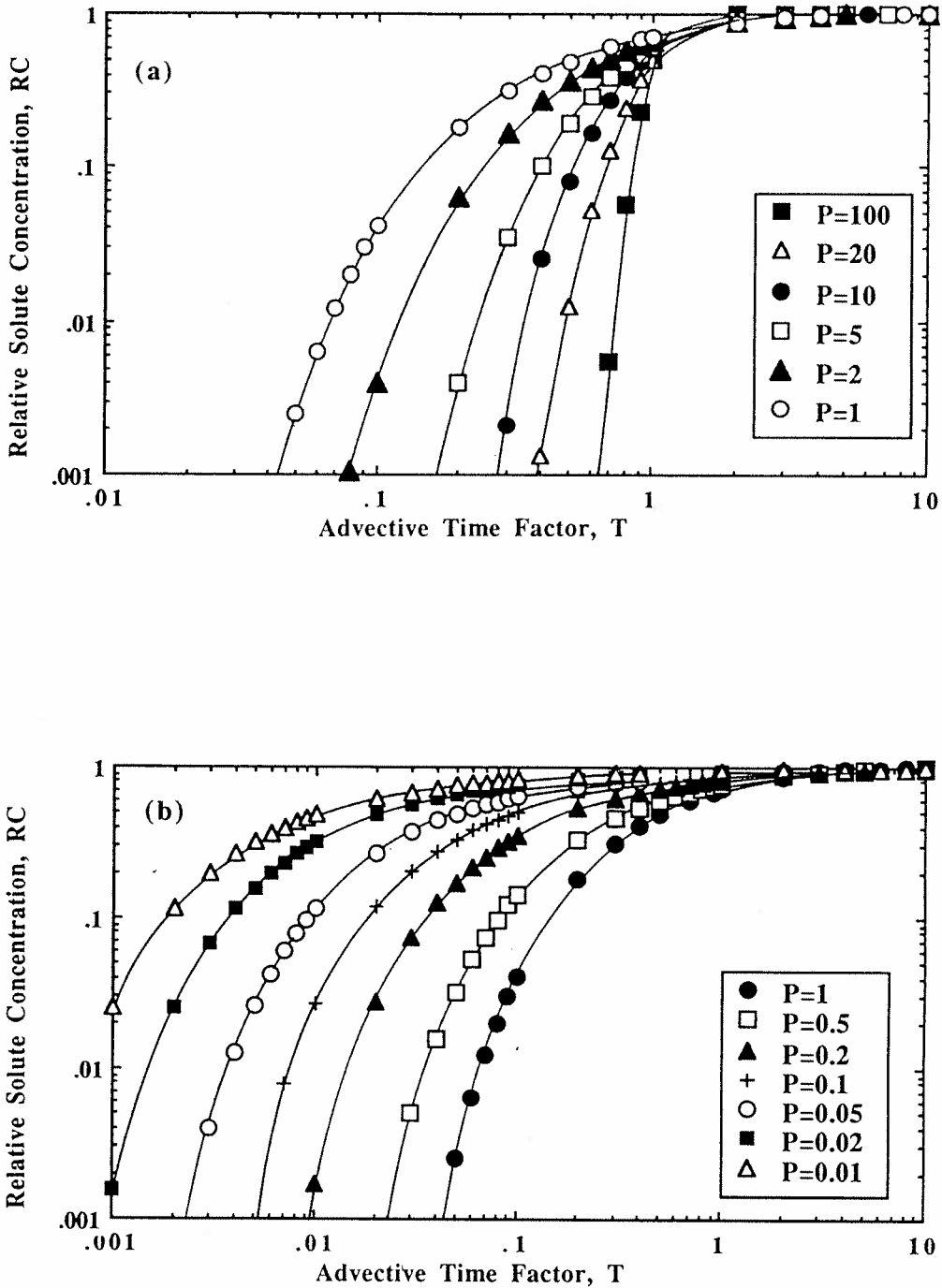


Fig. 4 - Advective time factor (Eq. 14) versus relative concentration ($=c_1/c_0$) for diffusion with positive advection as a function of Peclet number (Eq. 14): (a) high Peclet numbers; (b) low Peclet numbers [after SHACKELFORD, 1990; 1992].

Fig. 4 - Fattore tempo convettivo (Eq. 14) in funzione della concentrazione relativa (c_1/c_0) per diversi valori del numero di Peclet (Eq. 14) nel caso di diffusione con convezione positiva: (a) Numeri di Peclet elevati; (b) numeri di Peclet ridotti [da SHACKELFORD, 1990; 1992].

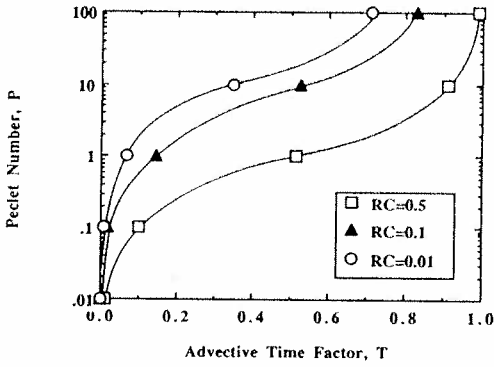


Fig. 5 - Advective time factor (Eq. 14) versus Peclet number (Eq. 14) as a function of relative concentration for diffusion with positive advection.

Fig. 5 - Fattore tempo convettivo (Eq. 14) in funzione del numero di Peclet (Eq. 14) per diversi valori di concentrazione relativa nel caso di diffusione con convezione positiva.

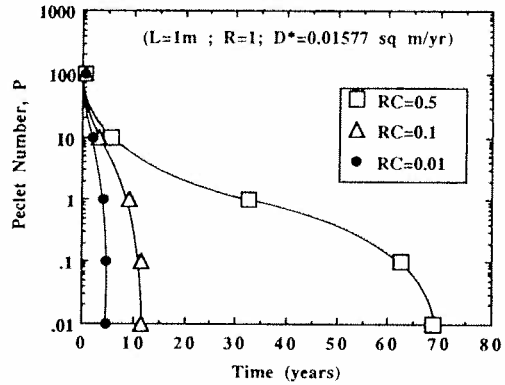


Fig. 6 - Breakthrough time versus Peclet number (Eq. 14) as a function of relative concentration for diffusion with positive advection.

Fig. 6 - Tempo di attraversamento in funzione del numero di Peclet (Eq. 14) per diversi valori di concentrazione relativa nel caso di diffusione con convezione positiva.

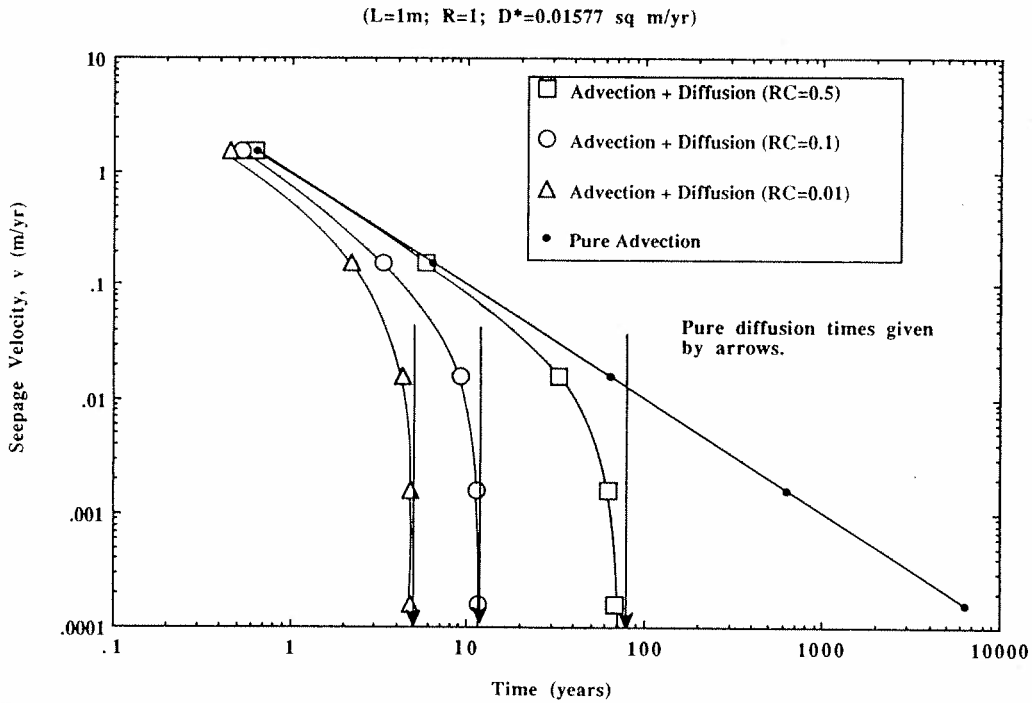


Fig. 7 - Breakthrough time as a function of barrier seepage velocity for pure diffusion, pure advection, and diffusion with positive advection [after SHACKELFORD, 1988].

Fig. 7 - Tempo di attraversamento in funzione della velocità di filtrazione attraverso la barriera nei casi di diffusione semplice, convezione semplice e diffusione con convezione positiva [da SHACKELFORD, 1988].

more time than under diffusive plus positive advective transport conditions, but less time than would be predicted under purely advective transport conditions. Since the best barrier that can be constructed under the current scenario is a diffusion-controlled barrier, barrier designs based solely on advective transport (i.e., Darcy's law) are not only incorrect but also are unconservative.

The obvious conclusion from this analysis is that a low permeability for a soil barrier is a *necessary*, but not *sufficient*, condition for the design of soil barriers under the influence of both advective (positive) and diffusive transport processes. Failure to account properly for the effect of diffusion at low flow rates can lead to potentially dangerous consequences.

As with pure diffusive transport conditions, it may be more practical to evaluate the transport of contaminants through a barrier in terms of mass flux, as opposed to concentration, for the case of diffusion with positive advection. This evaluation has been presented by SHACKELFORD [1992] in terms of a dimensionless relative flux, RF, defined as follows:

$$RF = \frac{J}{qc_0} = \frac{J_a + J^*}{qc_0} = \frac{\frac{J_a}{c_0} + \frac{J^*}{c_0}}{q} \quad (30)$$

where J_a is given by combining Eqs. (1) and (12), J^* is given by Eq. (23), and qc_0 represents the steady-state advective transport of the contaminant at c_0 concentration. Values of RF versus the advective time factor, T , for high and low Peclet numbers are plotted in Figs. 8a and 8b, respectively. For advective-dominated transport conditions (high P values), the diffusive flux, J^* , provides a negligible contribution to the total solute flux, J , and the RF value gradually increases to a value of 1.0, as shown in Fig. 8a. As diffusion becomes more significant relative to advection (i.e., as P decreases), the advective flux becomes negligible relative to the diffusive flux and, at early times, T , the value of RF exceeds unity. However, as steady-state transport conditions are approached (i.e., at long times), the value of RF necessarily must decrease to 1.0 corresponding to the advective steady-state mass flux, qc_0 .

For the steady-state conditions given by Eq. (17), the total solute flux (advective plus diffusive flux) can be evaluated by differentiating Eq. (18) with respect to « x », letting $x=L$, and substituting the result into Eq. (6), or:

$$J = nv \frac{c_0 \exp(P) - c_1}{\exp(P) - 1} \quad (31)$$

In terms of relative solute flux, Eq. (30), the total solute flux, Eq. (31), is represented as follows:

$$RF = \frac{\exp(P) - (c_1/c_0)}{\exp(P) - 1} = \frac{\exp(P) - RC}{\exp(P) - 1} \quad (32)$$

Relative flux values determined with Eq. (32) for $c_1=0$ are plotted for comparison in Fig. 9. For diffusion-dominated transport, the RF value from Eq. (32) is almost twice the RF peak value given by Eqs. (23) and (30) for the case of pure diffusion. As advection becomes more significant, the steady-state and transient solutions give the same results for RF in the case of long-term conditions.

The relative solute flux, RF, as given by Eq. (32), also is plotted versus Peclet number, P , for several different ratios of relative concentrations, RC ($=c_1/c_0$), in Fig. 9. For the diffusion plus positive advection scenario, $RF \rightarrow 1$ for $P \rightarrow \infty$ (i.e., the total solute flux is mainly advective, whereas for $P=0$ (Fig. 9b), $RF \rightarrow \infty$ (i.e., the total solute flux is mainly diffusive) and tends to approach the values given by Eq. (27). Of course, when $c_1/c_0=1$, only advective flux is possible and, therefore, $RF=1$ for all P values.

As illustrated in Fig. 9, mass flux values, based on Eq. (32) for the case of steady-state conditions with constant concentrations at the upper and lower barrier surfaces, are significantly greater, when RC is maintained low, than the maximum short-term flux values based on the analytical solution for the transient problem shown in Fig. 8. For example, for $P=0.05$ ($1/P=20$) and $RC=0$, RF for the steady-state conditions (Fig. 9a) is approximately 20, whereas the maximum RF for the transient conditions (Fig. 8b) is only about 10. Therefore, the use of transient equations to describe the long-term mass flux is unconservative for the case of diffusion with positive advection when a flushing action is apparent at the lower or external boundary of barrier.

7. Diffusion with negative advection

The case of diffusion with negative advection (see Fig. 1) is becoming significant from a practical standpoint as more remediation schemes are requiring the placement of a slurry wall around an existing contaminated area integrated by internal dewatering systems. This case was previously analyzed by GRAY and WEBER [1984] simply by utilizing Eq. (12) with a positive hydraulic gradient, i ($=\Delta h/L$), resulting in an inward (negative) seepage velocity or advective flux and in an outward (posi-

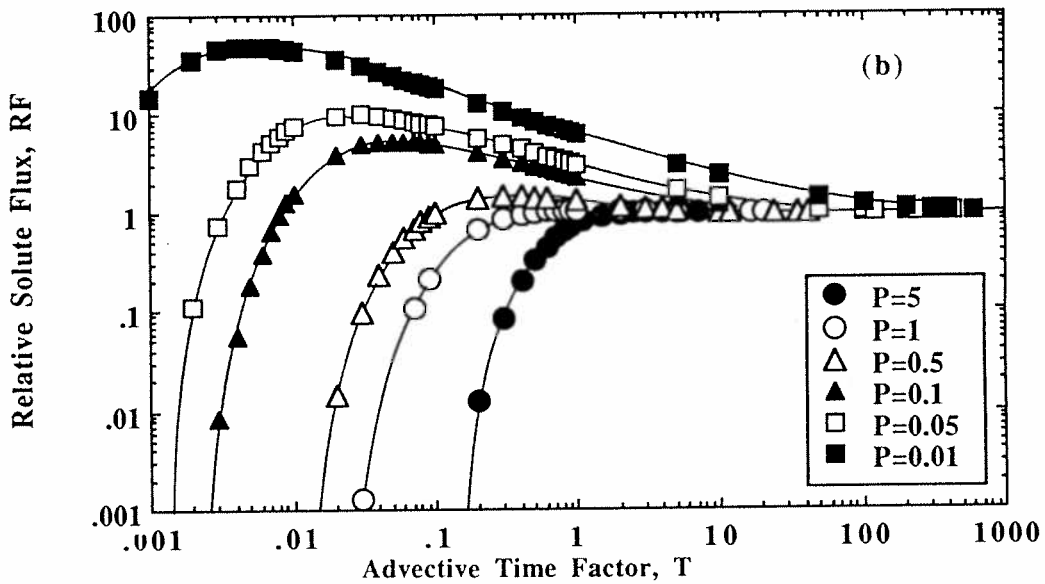
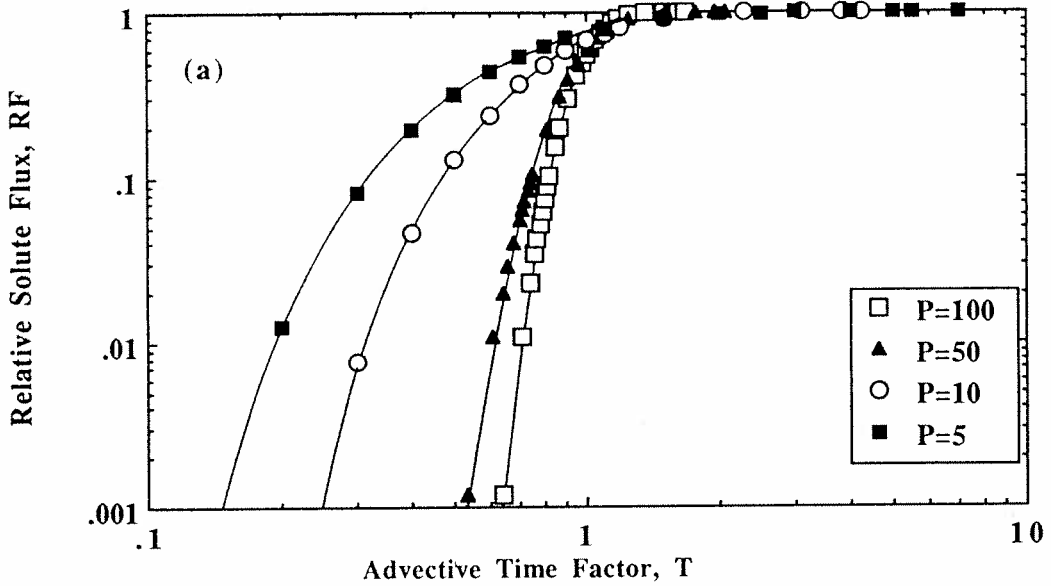


Fig. 8 - Advective time factor (Eq. 14) versus relative solute flux (Eq. 30) for diffusion with positive advection as a function of Pelet number (Eq. 14): (a) high Pelet numbers; (b) low Pelet numbers [after SHACKELFORD, 1990, 1992].

Fig. 8 - Fattore tempo convettivo (Eq. 14) in funzione del flusso relativo di soluto (Eq. 30) nel caso di diffusione con convezione positiva per diversi valori del numero di Pelet (Eq. 14): (a) numeri di Pelet elevati; (b) numeri di Pelet ridotti [da SHACKELFORD, 1990, 1992].

Diffusion with Positive and Negative Advection

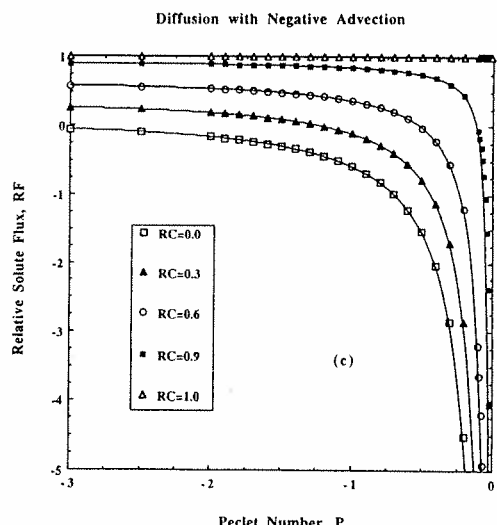
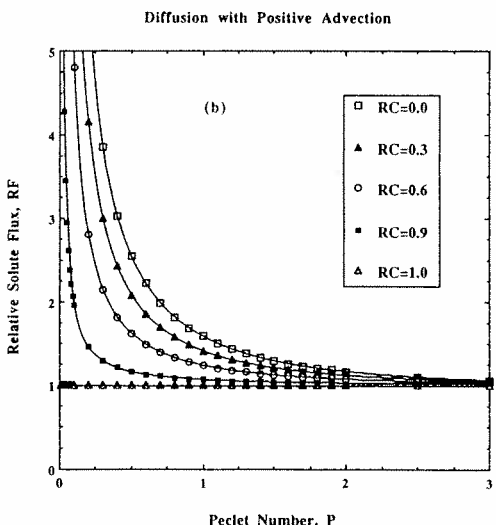
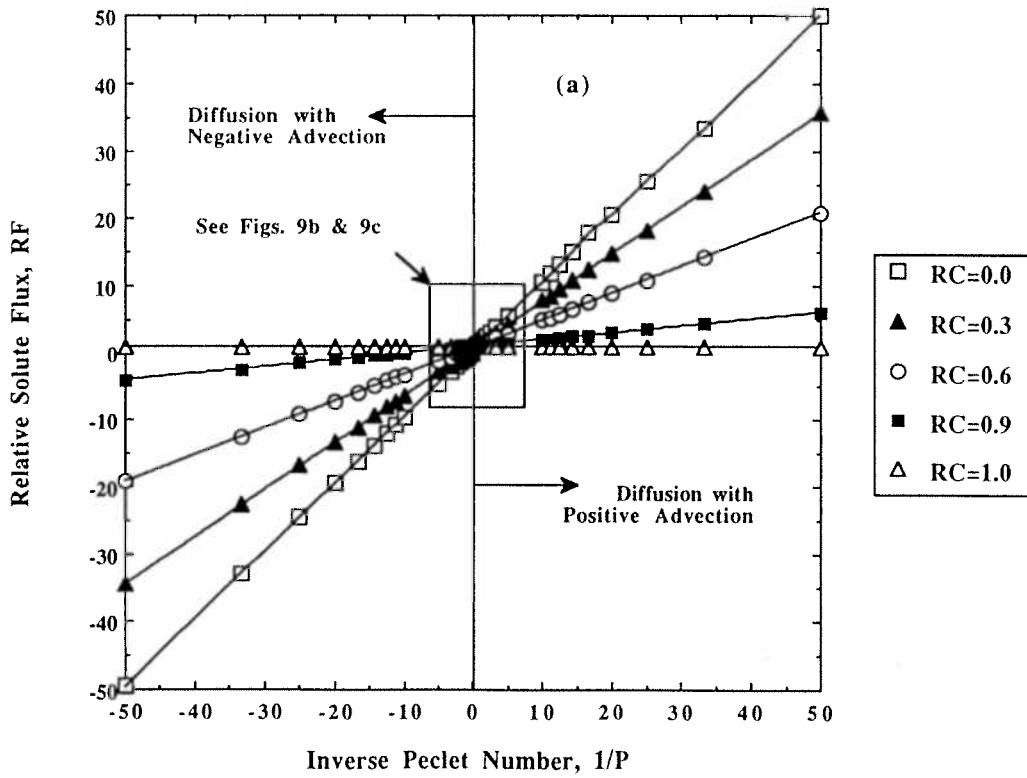


Fig. 9 - Relative solute flux (Eq. 30) as a function of relative concentration ($= c_1/c_0$) for steady-state transport conditions: (a) diffusion with both positive and negative advection; (b) diffusion with positive advection; (c) diffusion with negative advection.

Fig. 9 - Flusso relativo di soluto (Eq. 30) in funzione della concentrazione relativa ($= c_1/c_0$) per condizioni stazionarie: (a) diffusione con convezione positiva e negativa; (b) diffusione con convezione positiva; (c) diffusione con convezione negativa.

tive) diffusive flux. Their analysis is presented in the present study in terms of the effect of the Peclet number, P , on the relative solute concentration, RC , at $x=L$, as a function of the advective time factor, T , as shown in Fig. 10. The values of both T and P are negative in this case since the value of v (or q) is negative; i.e., a negative value of T will equate to positive values for elapsed time, t , since v is also negative, whereas a negative value of P simply means that advection is in a direction opposite to diffusion (see Eq. 14). As expected, the values for RC decrease as the absolute value of P increases (i.e., as P becomes more negative). However, in many cases, the values for RC in Fig. 10 represent concentrations which may exceed allowable limits and, therefore, failure to account for diffusion in this scenario may result in unconservative designs.

In terms of flux, the total solute flux, J , is still the sum of the advective flux and diffusive flux in accordance with Eq. (6), but in this case the numerical value of the advective flux, J_a , becomes negative due to the negative seepage velocity.

The significance of the negative advective flux is illustrated in Fig. 11, where the advective, diffusive, and total solute fluxes normalized with respect to the containment concentration, c_0 , are plotted versus time for a 1-m thick barrier ($R=1$; $n=0.5$; $K=0.03154$ m/yr; $D^*=0.01577$ m²/yr; $i=0.2$). The plots in Fig. 11 are in terms of real time and, therefore, t is positive. In this case, the seepage velocity is -0.01262 m/yr and it is not sufficient to stop the outward flux due to diffusion in the considered range of time, i.e., the total (net) solute flux is still in the positive x -direction. However, increasing the inward hydraulic gradient (i.e., as the Peclet number, P , becomes increasingly more negative), the net outward flux can be reduced significantly, as shown in Fig. 12. The results in Fig. 12 are plotted in terms of the dimensionless relative flux, RF (Eq. 30).

The steady-state condition for diffusion with negative advection can be analyzed simply by considering negative Peclet numbers (i.e., $v < 0$) in Eqs. (18) and (32). As shown in Fig. 9c, as P becomes increasingly more negative, $RF \rightarrow RC$. Also indicated in Fig. 9c, the total steady-state solute flux, J , can be either negative (inward) corresponding to positive RF values or positive (outward) corresponding to negative RF values. However, RF can never be algebraically higher than pure advective flux in the inward direction (i.e., $RF \leq 1$).

The values of P at which RF changes algebraic sign can be determined by setting RF equal to zero in Eq. (32) and solving for P , or $P = I_n(RC)$. These values of P can be used to determine the head difference, Δh (through the definition of P (Eq. 14) required to

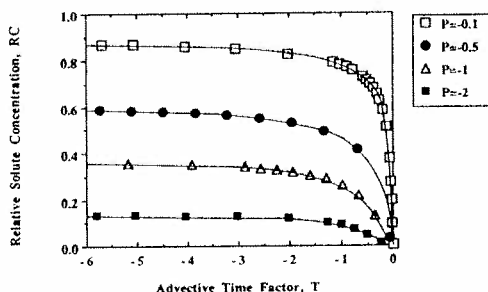


Fig. 10 - Advective time factor (Eq. 14) versus relative concentration ($= c_1/c_0$) for diffusion with negative advection as a function of Peclet number (Eq. 14).

Fig. 10 - Fattore tempo convettivo (Eq. 14) in funzione della concentrazione relativa ($= c_1/c_0$) per diversi valori del numero di Peclet (Eq. 14) nel caso di diffusione con convezione negativa.

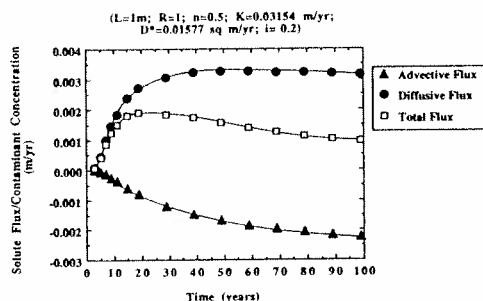


Fig. 11 - Components of total flux as a function of breakthrough time for case of diffusion with negative advection.

Fig. 11 - Componenti del flusso totale in funzione del tempo di attraversamento per il caso di diffusione con convezione negativa.

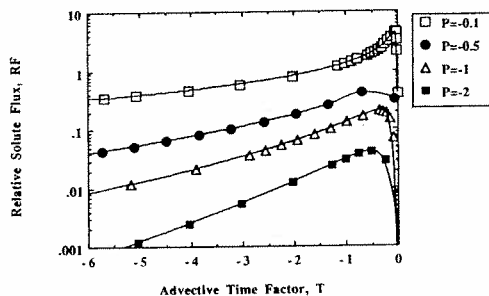


Fig. 12 - Advective time factor (Eq. 14) versus relative solute flux (Eq. 30) for diffusion with negative advection as a function of Peclet number (Eq. 14).

Fig. 12 - Fattore tempo convettivo (Eq. 14) in funzione del Flusso relativo di soluto (Eq. 30) per diversi valori del numero di Peclet (Eq. 14) nel caso di diffusione con convezione negativa.

stop the net outward flux. Higher Δh values determine a net inward flux (i.e., a positive RF value).

The equilibrium, steady-state (long-term) concentrations resulting from this case have been analyzed by MANASSERO [1991] and MANASSERO and PASQUALINI [1992] by letting $RF=0$ in Eq. (32) or $J=0$ in Eq. (6), and solving for the concentration after substituting for respective advective and diffusive fluxes, as follows:

$$\left. \begin{aligned} J_a &= -J^* \\ vc &= D^* \frac{dc}{dx} \\ \int_{c_0}^{c_1} \frac{dc}{c} &= \frac{v}{D^*} \int_0^L dx \end{aligned} \right\} \quad (33)$$

or:

$$RC = \frac{c_1}{c_0} = \exp\left(\frac{vL}{D^*}\right) = \exp(P) \quad (34)$$

The results of this analysis are presented in Fig. 13.

The results (in terms of RC), presented in Eq. (34) and Fig. 13, are the same as the long-term RC values in Fig. 10; i.e., if no flushing action exists on the external barrier surface, contaminant mass flux goes to zero regardless of the boundary conditions. On the other hand, long-term conditions are provided by Eq. (18) in terms of concentration and by Eq. (32) in terms of mass flux for the condition when a flushing action exists on the external barrier surface.

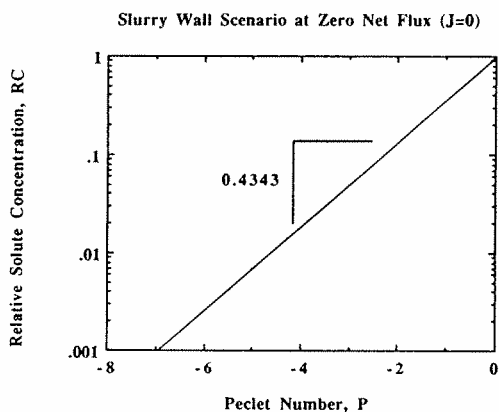


Fig. 13 - Peclet number (Eq. 14) versus relative concentration ($=c_1/c_0$) for zero net mass flux across soil barrier [after MANASSERO, 1991; MANASSERO and PASQUALINI, 1992].

Fig. 13 - Numero di Peclet (Eq. 14) in funzione della concentrazione relativa ($=c_1/c_0$) nel caso di flusso di soluto nullo attraverso la barriera minerale [da MANASSERO, 1991; MANASSERO e PASQUALINI, 1992].

8. Measurement of effective diffusion coefficients

Both steady-state and transient methods also can be used to measure effective diffusion coefficients, D^* , of miscible contaminants for use in the analyses previously described. For example, SHACKELFORD [1991] and SHACKELFORD and DANIEL [1991 a] describe several methods for the laboratory measurements of D^* , including the half-cell method, the steady-state method, and both column and reservoir methods with constant and decreasing source concentrations.

Although there are both advantages and disadvantages to each method, the single reservoir with decreasing source concentration (SRDC) method is relatively easy to use and the experimental setup and boundary conditions are similar to environmental applications, in which contaminants are contained by soil mineral barriers [SHACKELFORD, 1991; VAN REES *et al.*, 1991]. In the SRDC method, a reservoir of liquid (e.g., leachate) containing initial concentrations, c_0 of one or more solutes of interest (e.g., Cl^- , Pb^{2+}) is placed on top of a cell of soil, as shown in Fig. 14a. The difference in solute concentration between the reservoir and the pore liquid of the soil establishes a concentration gradient for diffusion of solutes into the soil. The decrease in reservoir concentration with time, as well as the resulting profile of solute concentration with depth in the soil at the end of the test, are analyzed with an appropriate analytical solution to Eq. (19) to evaluate D^* . For example, SHACKELFORD and DANIEL [1991 b] and SHACKELFORD *et al.* [1989] used the SRDC method to measure effective diffusion coefficients of inorganic metals (e.g., Cd^{2+} and Zn^{2+}), as well as chloride (Cl^-), in compacted clay soils typically considered for waste containment barriers. Some typical profiles and results from their tests are shown in Fig. 14.

As shown in Figs. 14b and 14c, the values of D^* for inorganic metals determined from reservoir concentrations typically are greater than the values of D^* determined from concentration profiles in the soil at the end of the test [see SHACKELFORD and DANIEL, 1991b; VAN REES *et al.*, 1991]. Therefore, the D^* values determined from the soil concentration profiles generally are considered to be more reliable, although the determination of D^* values from reservoir concentrations usually is easier and results in more consistent data. In such cases, barrier designs, based on measured D^* values determined from the reservoir concentrations usually will be conservative.

Several other test considerations are important for the correct evaluation of effective diffusion coefficients. For example, for unsaturated soils, such as compacted clay, consideration must be given to the possibility of advective migration of contaminants

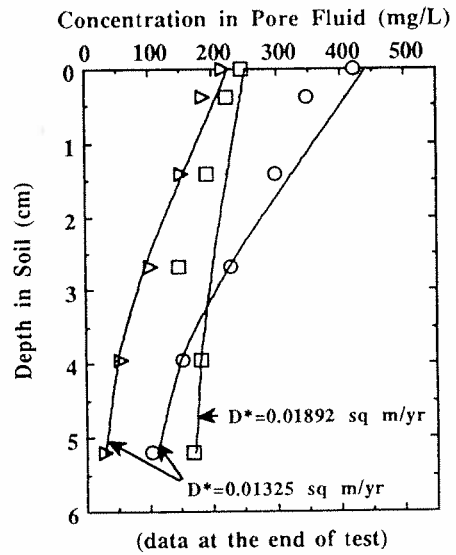
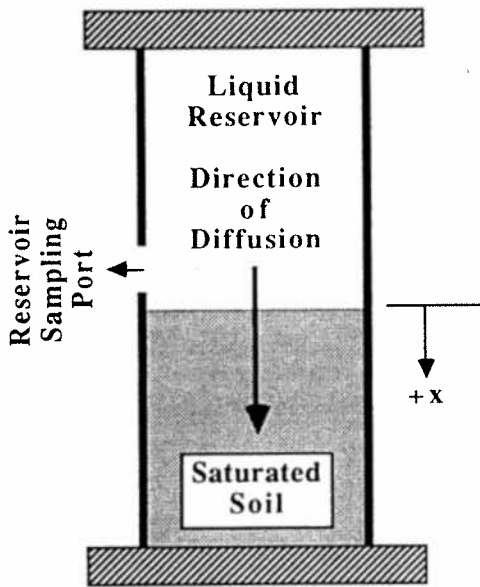
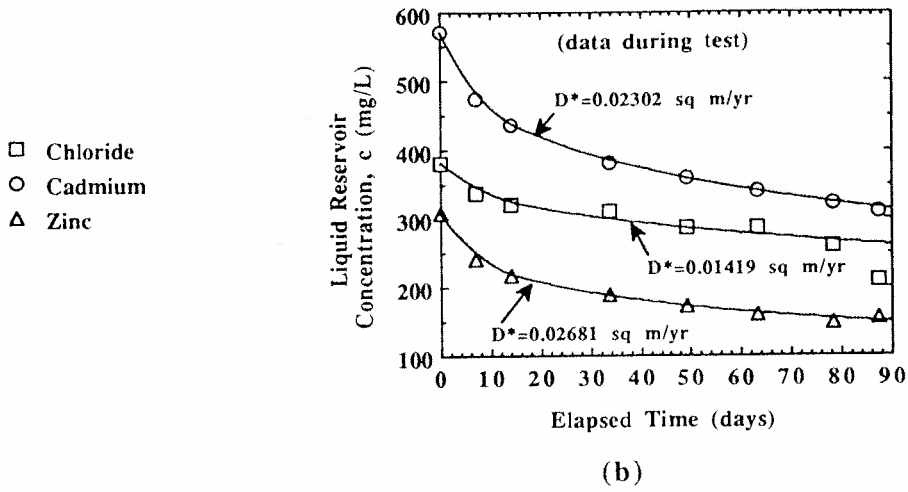


Fig. 14 - Single-reservoir with decreasing source concentration diffusion test: (a) schematic test set-up; (b) liquid reservoir concentrations as a function of time; (c) pore fluid concentrations versus depth in soil [after SHACKELFORD and DANIEL, 1991a, b; SHACKELFORD, 1991].

Fig. 14 - Prova di diffusione in laboratorio con il metodo del serbatoio singolo e concentrazione del contaminante decrescente: (a) schema della prova; (b) concentrazione del liquido nel serbatoio in funzione del tempo; (c) concentrazione nel liquido interstiziale del campione di terreno alle varie profondità [da SHACKELFORD e DANIEL, 1991a, b; SHACKELFORD, 1991].

during the test due to the suction in the soil. In addition, an evaluation of the retardation factor, R , is required for correct measurements of the effective diffusion coefficient, D^* , of adsorbing solutes, such as the toxic heavy metals (e.g., Cd^{2+} , Pb^{2+} , Zn^{2+}), in accordance with Eq. (19). These and other test considerations are covered in detail by SHACKELFORD [1991] and SHACKELFORD *et al.* [1989].

9. Illustrative design examples

One illustrative design example is presented for each of the three waste containment scenarios, shown in Fig. 1, to illustrate application of the concepts and utilization of the dimensionless charts presented in this paper. Although rather close to the real situations the considered cases are very simple and schematic and must be seen as a basic proposal for advancement and improvement of mineral barrier design which, up to now, has been only based on hydraulic conductivity considerations.

9.1. Pure diffusion

An area is confined with a soil-bentonite slurry wall during remedial work to provisionally store wastes. The reference chemical constituent for the wastes is assumed to be nonreactive ($R = 1$) chloride (Cl^-), which is present in the wastes at a concentration of 10 g/l. No hydraulic gradient exists across the barrier; therefore, this case corresponds to the pure diffusion scenario (Fig. 1). The soil-bentonite slurry wall is characterized by a porosity, n , of 0.7, and the effective diffusion coefficient (D^*) for chloride is taken as $0.01892 \text{ m}^2/\text{yr}$ [e.g., see SHACKELFORD, 1991]. The purpose of the design is to determine the barrier thickness required to limit the external concentration of chloride to the local regulatory value of 500 mg/l considering a two-year operational life (breakthrough time) of the waste disposal facility.

Therefore, the maximum relative solute concentration after two years is:

$$RC = \frac{c_1}{c_0} = \frac{500}{10000} = 0.05$$

Based on this value for RC , the diffusive time factor, T^* , from Fig. 3 is 0.12 and, from the definition of T^* given by Eq. (22), the following minimum value for the wall thickness is calculated:

$$L = \sqrt{\frac{D^*t}{RT^*}} = \sqrt{\frac{\left(0.01892 \frac{\text{m}^2}{\text{yr}}\right) \cdot (2\text{yr})}{(1)(0.12)}} = 0.56 \text{ m}$$

At the end of the provisional active period, the chloride mass flux number, FN , will be (see Fig. 3):

$$FN = \frac{J^* L}{nD^*c_0} = 0.225$$

and, therefore, the chloride mass flux is:

$$J^* = \frac{0.225 \left[(0.7) \left(0.01892 \frac{\text{m}^2}{\text{yr}} \right) \left(10 \frac{\text{g}}{\text{l}} \right) \left(1000 \frac{\text{l}}{\text{m}^3} \right) \right]}{0.56 \text{ m}} = 53 \frac{\text{g}}{\text{m}^2\text{yr}}$$

For the case where a flushing action due to natural groundwater flow maintains a constant external concentration of $c_1 = 500 \text{ mg/l}$, the following steady-state long-term mass flux of chloride can be calculated from Eq. (27):

$$J^* = -nD^* \left(\frac{c_1 - c_0}{L} \right) = (0.7) \left(0.01892 \frac{\text{m}^2}{\text{yr}} \right) \left[\frac{\left(0.5 \frac{\text{g}}{\text{l}} - 10 \frac{\text{g}}{\text{l}} \right) \left(1000 \frac{\text{l}}{\text{m}^3} \right)}{(0.56 \text{ m})} \right] = 225 \frac{\text{g}}{\text{m}^2\text{yr}}$$

A conservative operational thickness of 1 m is suggested in this case to account for uncertainties in design parameters and construction defects in the slurry walls.

9.2. Diffusion with Positive Advection

A one-meter thick compacted clay liner is used to contain an industrial liquid waste. The waste contains relatively high concentrations of chloride (Cl^-) and zinc (Zn^{2+}) among other chemical constituents. The hydraulic conductivity and porosity of the compacted clay liner are $5 \cdot 10^{-11} \text{ m/s}$ and 0.37, respectively. A hydraulic gradient of -1.33 and saturated conditions are assumed [see SHACKELFORD, 1992]. Based on these assumptions, the steady-state seepage velocity through the liner is:

$$v = -\frac{Ki}{n} = -\frac{\left(5 \cdot 10^{-11} \frac{\text{m}}{\text{s}} \right) (-1.33)}{0.37} = 1.8 \cdot 10^{-10} \frac{\text{m}}{\text{s}} = 0.005668 \frac{\text{m}}{\text{yr}}$$

where i is defined in the direction opposite to flow i.e., $i = \frac{dh}{dx}$.

The chemical properties of the chloride and zinc with the soil of interest are summarized in Table I. The first check concerns the short-term problem related to the chloride migration. The Peclet number for Cl^- is:

$$P = \frac{\left(0.005668 \frac{\text{m}}{\text{yr}}\right)(1.0\text{m})}{0.01892 \frac{\text{m}^2}{\text{yr}}} = 0.30$$

and, with $c_1/c_0 = 0.20$, the advective time factor, T , from Fig. 4b, is approximately 0.10. Therefore, the time required for the chloride concentration to reach the maximum allowable concentration is calculated from Eq. (14) as follows:

$$t = \frac{\text{RTL}}{v} = \frac{(1.0)(0.1)(1\text{m})}{0.005668 \frac{\text{m}}{\text{yr}}} = 17.6\text{yr}$$

If this duration is not sufficient, a treatment process in the waste stream is required to reduce the chloride concentration and/or the liner thickness must be increased.

Although the retardation factor for the zinc is 3, the allowable relative concentration of 0.05 is very low. The Peclet number for zinc is:

$$P = \frac{\left(0.005668 \frac{\text{m}}{\text{yr}}\right)(1.0\text{m})}{0.02681 \frac{\text{m}^2}{\text{yr}}} = 0.21$$

and, with $\text{RC} = 0.05$, the advective time factor, T , from Fig. 4b, is approximately 0.022. Therefore,

$$t = \frac{\text{RTL}}{v} = \frac{(3.0)(0.022)(1\text{m})}{0.005668 \frac{\text{m}}{\text{yr}}} = 11.7\text{yr}$$

which is lower than the time required for chloride. Therefore, zinc controls the design of this barrier for transient conditions. Also, note that the advective transit times for chloride and zinc based on Eq. (29) are 176 and 529 years, respectively, indicating the extremely unconservative results possible when diffusion is neglected in the analysis.

A long-term analysis for steady-state conditions can be performed assuming that the soil liner is underlain by a superficial aquifer (e.g., drainage layer) 1-m thick flowing horizontally at a rate, q , of 30 m^3/yr corresponding to a volumetric flushing flux, $Q (=qA)$, of 30 m^3/yr per meter.

The long-term pollutant concentration, c_1 , in the underlying aquifer (downstream of the landfill) can be assessed, as a first approximation, assuming that the solute concentration in the aquifer is constant with depth and that the solute transport mechanism in the aquifer is purely advection. This simplified analysis is appropriate only when both the aquifer and landfill liner thicknesses are much less (say 10%) than the average horizontal dimension of the landfill, l , in the direction parallel to the direction of the groundwater flow in the aquifer. Under these constraints, the contaminant mass balance across the liner-aquifer interface at steady-state conditions is given by:

$$c_1 \cdot Q = J \cdot l$$

which, upon substitution for the contaminant mass flux, J , given by Eq. (31), results in the following expression for the relative solute concentration:

$$\text{RC} = \frac{c_1}{c_0} = \frac{nl \exp(P)}{Q[\exp(P) - 1] + nl}$$

For a landfill length, l , of 100 m and the previously defined numerical values for the other parameters, the relative solute concentration for chloride (Cl^-) at steady-state conditions becomes:

$$\text{RC} = \frac{(0.37)\left(0.005668 \frac{\text{m}}{\text{yr}}\right)(100\text{m})\exp(0.3)}{\left(30 \frac{\text{m}^3}{\text{yr}}\right)\left[\exp(0.3) - 1\right] + (0.37)\left(0.005668 \frac{\text{m}}{\text{yr}}\right)(100\text{m})} = 0.026$$

which is much less than the allowable limit of 0.20 for chloride from Table I. For zinc (Zn^{2+}), the relative solute concentration at steady-state conditions is:

$$\text{RC} = \frac{(0.37)\left(0.005668 \frac{\text{m}}{\text{yr}}\right)(100\text{m})\exp(0.21)}{\left(30 \frac{\text{m}^3}{\text{yr}}\right)\left[\exp(0.21) - 1\right] + (0.37)\left(0.005668 \frac{\text{m}}{\text{yr}}\right)(100\text{m})} = 0.036$$

TABLE I - Chemical Properties used for the Example. [SHACKELFORD and DANIEL, 1991b]

Chemical constituent	Concentration in leachate c_0 (mg/l)	Allowable concentration c_1 (mg/l)	$\text{RC} = \frac{c_1}{c_0}$	D^* (m^2/yr)	R
Chloride (Cl^-)	1250	250	0.20	0.01892	1.0
Zinc (Zn^{2+})	100	5.0	0.05	0.02681	3.0

which is slightly less than the allowable limit for zinc of 0.05 from Table 1. Therefore, the allowable limits specified in Table 1 for the maximum concentrations of both Cl^- and Zn^{2+} in the underlying aquifer are not exceeded, indicating that the design of the soil barrier is satisfactory based on the assumptions and criterion of the analysis. In addition, the above analysis indicates that zinc also controls the design of the barrier in terms of long-term conditions.

9.3. Diffusion with Negative Advection

A vertical slurry wall is to be designed to confine cadmium (Cd^{2+}) with an average concentration, c_0 , of 1.95 mg/l. The concentration of Cd^{2+} in the static groundwater outside the barrier, c_1 , must be kept below the regulatory limit of 0.01 mg/l; therefore, $c_1/c_0 = 0.005$. The parameters of interest for the slurry wall design are as follows:

porosity, $n = 0.7$ effective diffusion coefficient $D^* = 0.009461 \text{ m}^2/\text{yr} = 3 \cdot 10^{-10} \text{ m}^2/\text{s}$; and hydraulic conductivity, $K = 10^{-9} \text{ m/s}$.

For the RC value of 0.005, the Peclet number from Fig. 13 is -5.3 . From the definition of the Peclet number, Eq. (14), with respect to the scenario for diffusion with negative advection shown in Fig. 1,

$$P = \frac{vL}{D^*} = \left(-\frac{Ki}{n} \right) \left(\frac{L}{D^*} \right) = \left(-\frac{K\Delta h}{nL} \right) \left(\frac{L}{D^*} \right) = -\frac{K\Delta h}{nD^*}$$

Therefore, the total head difference which must be maintained across the wall (e.g., by pumping) is:

$$\Delta h = -\frac{nPD^*}{K} = -\frac{(0.7)(-5.3)\left(3 \cdot 10^{-10} \frac{\text{m}^2}{\text{s}}\right)}{\left(1 \cdot 10^{-9} \frac{\text{m}}{\text{s}}\right)} = 1.1\text{m}$$

The plot shown in Fig. 15, [see MANASSERO and PASQUALINI, 1992] can be used to evaluate the slurry wall thickness neglecting the flow through the base of the

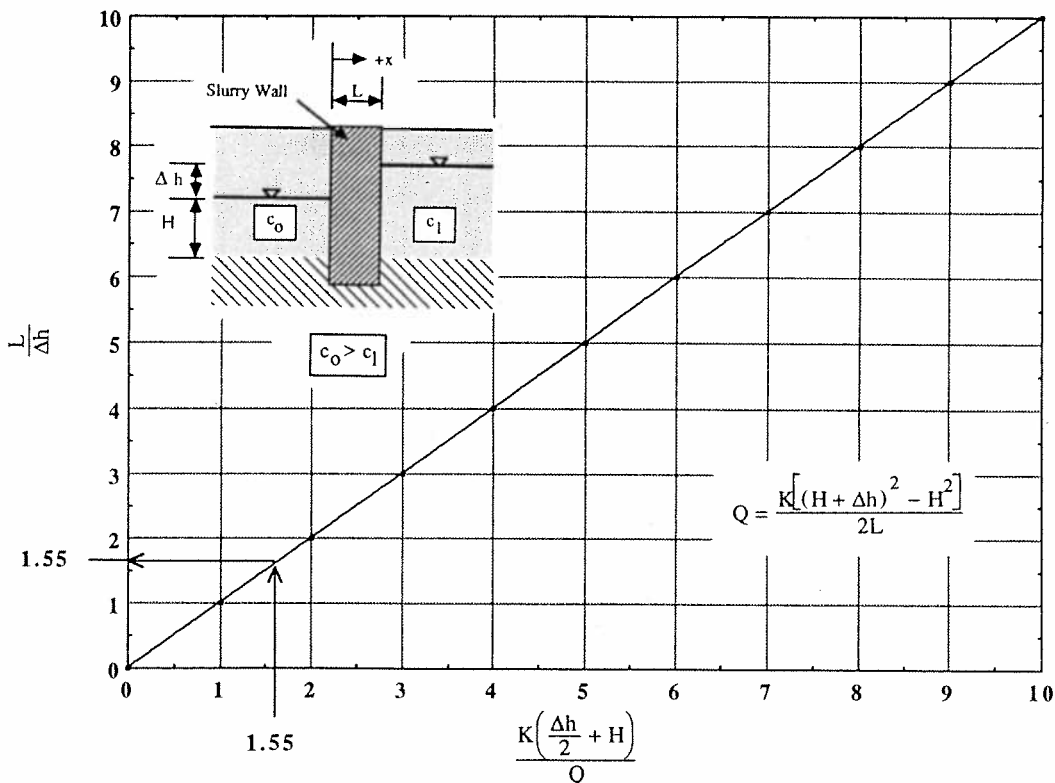


Fig. 15 - Slurry wall thickness design in the case of diffusive solute migration control via reverse hydraulic gradient [after MANASSERO, 1991; MANASSERO and PASQUALINI, 1992].

Fig. 15 - Definizione dello spessore dei diaframmi di contenimento nel caso di controllo del processo di diffusione del soluto per mezzo di un gradiente idraulico inverso [da MANASSERO, 1991; MANASSERO e PASQUALINI, 1992].

wall which can be minimized by increasing the embedment depth. If the dewatering and treatment systems at the site are able to pump and treat $1 \cdot 10^{-8} \text{ m}^3/\text{s}$ per meter of containment barrier, and if the distance, H , between the piezometric surface within the confined area and the underlying confining layer is 15 m, then:

$$\frac{K \left(\frac{\Delta h}{2} + H \right)}{Q} = \frac{\left(1 \cdot 10^{-9} \frac{\text{m}}{\text{s}} \right) \left(\frac{1.1 \text{m}}{2} + 15 \text{m} \right)}{\left(1 \cdot 10^{-8} \frac{\text{m}^3}{\text{s}} \right)} \cong 1.55$$

and

$$\frac{L}{\Delta h} \cong 1.55 \quad \text{or} \quad L \cong (1.55) (1.1 \text{ m}) \cong 1.7 \text{ m}$$

The power of the dewatering system must be increased if a thinner wall is required.

10. Summary and conclusions

The role of diffusion in contaminant migration through soil (mineral) barriers has been outlined with respect to three different waste containment scenarios: (1) pure diffusion (no seepage flow); (2) diffusion with positive advection (i.e., steady-state solvent (water) flow in the same direction as diffusion); and (3) diffusion with negative advection (i.e., steady-state solvent (water) flow in the opposite direction as diffusion). In each of the three scenarios, the pollutant concentration inside the barrier (upper boundary) has been kept constant in all of the models considered. However, for the external surface of the containment barrier (lower boundary), two different, simplified boundary conditions are considered. The first lower boundary condition is used to analyze transient conditions and assumes that the pollutant concentration is equal to zero at an infinite distance from the barrier at all times and can be applied reasonably well for short-term conditions only when the external groundwater is in static or quasi-static conditions. This boundary condition has been found to be conservative for all cases considered in terms of the time required for a contaminant to break through the barrier (i.e., transit time).

The second lower boundary condition considered refers to steady-state or long-term conditions, assuming a constant concentration just outside the barrier surface. When there is a significant flow component tangential to the external surface of the barrier (e.g., a flushing action from an underlying aquifer or drainage layer), the analysis in terms of contaminant mass flux becomes increasingly more conservative as the external barrier concentration approaches zero.

Based on the analyses presented in this paper, diffusion of contaminants through low-permeability soil (mineral) barriers is a significant, if not dominant, transport process. The significance of diffusion to the overall migration of contaminant increases as the seepage velocity decreases. In the limit (i.e., as the seepage velocity approaches to zero), the migration of contaminants approaches the case of pure diffusive transport. Even if the seepage velocity is zero, release rates of contaminants via diffusive transport can be high, particularly when relatively thin barriers are used to contain high concentrations of extremely toxic pollutants. Therefore, a low-permeability barrier is a *necessary*, but not *sufficient*, condition for the safe containment of contaminants. Failure to account for diffusive migration of contaminants is not only incorrect, but also is unconservative, and can lead to potentially dangerous consequences in many cases.

The single reservoir, decreasing source concentration method for measuring effective diffusion coefficients on laboratory samples for waste containment barriers is briefly described, and several references are provided for additional details of various measurement techniques. Design examples are presented to illustrate applications of the dimensionless design charts and to illustrate the relative influences of the various parameters affecting contaminant migration times and fluxes through the barrier systems.

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TRADUZIONE

Il ruolo della diffusione molecolare nella migrazione degli inquinanti attraverso le barriere minerali

SOMMARIO

Nell'articolo viene evidenziata la fondamentale importanza della diffusione molecolare nell'ambito dei fenomeni che governano la migrazione degli inquinanti attraverso le barriere minerali (rivestimenti di argilla compattata per depositi di sostanze inquinanti, diaframmi plastici per il confinamento di siti contaminati, ecc.). In particolare sono stati sviluppati gli aspetti riguardanti la definizione del fenomeno di trasporto per diffusione attraverso i mezzi porosi, l'importanza relativa dei vari parametri che intervengono nelle equazioni che descrivono la migrazione degli inquinanti ed il significato delle varie ipotesi adottate nei modelli di calcolo per il dimensionamento delle barriere minerali.

Inoltre vengono presentati dei grafici che utilizzano parametri addizionali allo scopo di sottolineare l'importanza del trasporto per diffusione attraverso le barriere minerali, sia in presenza di flusso stazionario sia in presenza di flusso transitorio, per tre diverse condizioni idrauliche al contorno che comportano rispettivamente: (1) diffusione semplice; (2) diffusione e convezione nella stessa direzione (diffusione con convezione positiva); (3) diffusione e convezione in direzioni opposte (diffusione con convezione negativa). Tali grafici di progetto consentono inoltre di determinare le caratteristiche fondamentali di una barriera per il confinamento di sostanze contaminanti sulla base delle concentrazioni a monte ed a valle della stessa oppure del flusso di massa ammissibile degli inquinanti verso l'esterno dell'opera di confinamento.

Le analisi riportate mostrano come una bassa conducibilità idraulica (permeabilità) della barriera sia un requisito necessario ma non sufficiente per una buona efficienza della barriera stessa.

Pertanto, trascurare il contributo della diffusione molecolare degli inquinanti in fase di progettazione può comportare un dimensionamento estremamente poco conservativo.

Nella nota viene mostrato come l'ipotesi di flusso stazionario del solvente (acqua) e le altre condizioni al contorno adottate nelle analisi sono indubbiamente approssimazioni semplificative delle condizioni reali, ma d'altro canto sono utili per ottenere valutazioni relativamente semplici e spedite delle prestazioni delle barriere in esame. Nell'utilizzo dei modelli analitici proposti vengono costantemente definite e sottolineate le ipotesi ed i parametri di input che comportano risultati di tipo conservativo.

Infine viene brevemente illustrato un metodo di laboratorio per la misura sperimentale del coefficiente di diffusione e, quindi, viene discussa ed esemplificata l'utilizzazione dei valori misurati nel dimensionamento delle barriere minerali.

1. Introduzione

Durante l'ultimo decennio numerosi studi hanno evidenziato nella diffusione un fenomeno di migrazione degli inquinanti significativo, se non prevalente, nel caso di terreni a grana fine, tipicamente impiegati per la realizzazione di barriere minerali (rivestimenti di argilla compattata, diaframmi plastici, ecc.) per il contenimento di materiali contaminanti [GOODALL e QUIGLEY, 1977; DESAULNIERS et al., 1982; 1986; CROOKS e Quigley, 1984; QUIGLEY e ROWE, 1986; QUIGLEY et al., 1987; JOHNSON et al., 1989]. Ne consegue che una bassa conducibilità idraulica è un requisito necessario ma non sufficiente per assicurare una adeguata efficienza delle barriere minerali. Lo scopo di questa nota è di evidenziare il ruolo imprescindibile della diffusione nell'ambito dei fenomeni di migrazione degli inquinanti attraverso le barriere minerali impiegate per il contenimento dei rifiuti; a tal fine vengono presentati i risultati di alcune analisi esemplificative effettuate per diverse condizioni al contorno di tipo semplificato.

2. Fenomeni di propagazione degli inquinanti

In assenza di fenomeni di flusso accoppiato (quali l'osmosi) la mi