

# Diffusion of Contaminants Through Waste Containment Barriers

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The steady-state and transient equations describing the process of diffusion in free (aqueous) solution are presented. Four types of free-solution diffusion coefficients are identified with respect to the systems used for their measurement. The free-solution diffusion coefficient is shown to be a function of several factors, including the temperature, viscosity, and dielectric constant of the solution; the radius and valence of the diffusing chemical species; and the equilibrium chemistry of the solution. Several modifications must be made to the free-solution diffusion equations in order to describe diffusion in soil. The modifications result from the reduced cross-sectional area and the longer and more tortuous pathways experienced by solutes diffusing in soil. In addition, some solutes may be subject to reversible sorption reactions during transport through the soil. As a result of these effects, diffusion in soil is slower than diffusion in free solution. The equations describing diffusion in soil are used to indicate the significance of diffusive transport of contaminants through fine-grained soil barriers. For waste containment barriers, the significance of diffusive contaminant transport is described with respect to three flow conditions. The significance of diffusion increases as the seepage velocity decreases. As a result, the best waste containment barrier is one in which diffusion controls the transport process. However, the rate of contaminant transport through waste containment barriers may still be relatively rapid even if diffusion is the only active transport mechanism, especially when relatively thin barriers are built to contain relatively high concentrations of contaminants.

Several factors affect the transport of contaminants through fine-grained soil barriers (e.g., clays). The most widely recognized factor is probably the hydraulic conductivity (permeability) of the soil. Considerable research has been performed to determine the permeability of soils used for waste containment barriers. However, growing evidence points to molecular diffusion as the principal mechanism of contaminant transport in fine-grained barrier materials (1-8). This evidence, coupled with the concern for the deleterious effects of minute concentrations of contaminants in groundwater, has increased the importance of considering diffusion as a transport process in the design of waste containment barriers.

The purposes of this paper are to review the concept of diffusion as a transport process and to describe the effects of diffusion on the transport of contaminants through fine-grained soil barriers used for the containment of toxic wastes. Several modifications to Fick's laws of diffusion are shown to be required for a more realistic representation of the process of diffusion, not only in free solutions but also in soils. Also, diffusion through soil barriers is shown to be an important, if not dom-

inant, transport process in soil. The appropriate equations for modeling both advective and diffusive transport through waste containment barriers are presented. The need to account for diffusion of contaminants through waste containment barriers is illustrated with the aid of several examples.

## DIFFUSION IN FREE SOLUTION

Diffusion is a fundamental, irreversible process whereby matter is transported spontaneously from one part of a system to another as a result of random molecular motions (9,10). These random molecular motions result in the net transport of a chemical species (e.g., ion, molecule) from a region of higher concentration to a region of lower concentration. As a result, diffusion may be thought of as the transport of a chemical species because of a gradient in its concentration.

### Types of Diffusion Coefficients

There are essentially four different types of diffusion coefficients: (a) self-diffusion, (b) tracer diffusion, (c) salt diffusion, and (d) counter- or interdiffusion. The type of diffusion coefficient that is measured depends on the system used to measure it. The four systems that describe the four types of diffusion coefficients are schematically represented in Figure 1, in which sodium chloride (NaCl) or potassium chloride (KCl) (or both) is assumed to be the diffusing compound.

In self-diffusion [Figure 1(a)], each half-cell of the system initially contains an equal concentration of sodium chloride (NaCl). However, in one half-cell, a small amount of the sodium,  $\text{Na}^+$ , has been replaced by its isotope,  $^{22}\text{Na}^+$ . When the two half-cells are connected, diffusion of both  $\text{Na}^+$  and its isotope,  $^{22}\text{Na}^+$ , occurs, but in opposite directions, owing to the small concentration gradients of each species. Because the concentration gradient is extremely small, the movements of the radioactive tracer ions ( $^{22}\text{Na}^+$ ) and the  $\text{Na}^+$  ions are not tied to that of the ions of opposite sign (i.e.,  $\text{Cl}^-$ ), and the tracer ions may be considered to be moving relative to a stationary background of nondiffusing ions (9). This movement of the tracer ions is termed *self-diffusion*, and the diffusion coefficient describing it is called the *self-diffusion coefficient*. Actually, this system does not depict true self-diffusion. In true self-diffusion, the initial system would contain two half-cells, each with equal concentrations of NaCl but without any isotopically different species. In such a system, the movement of the molecules would be truly random, but the motion of the molecules could never be traced. Therefore, the true

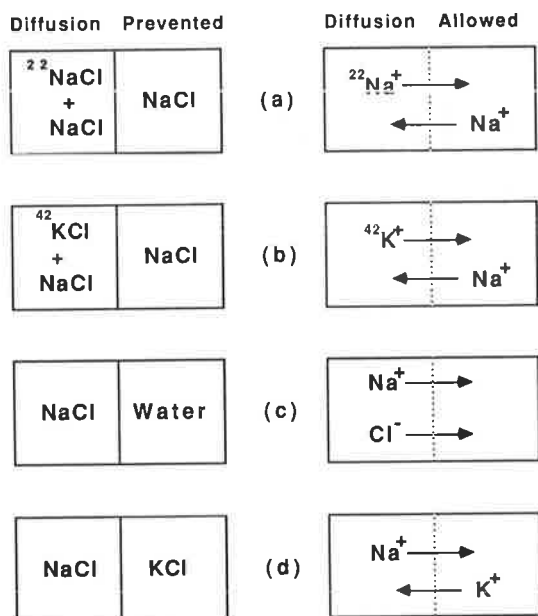


FIGURE 1 Schematic representation of diffusion cells for different systems: (a) self-diffusion, (b) tracer diffusion, (c) salt diffusion, and (d) counterdiffusion or interdiffusion [after Li and Gregory (13)].

self-diffusion system is approximated by the introduction of the isotopic (tracer) species.

Tracer diffusion is the same as self-diffusion in all respects except that the isotopic species is of a different element. For example, consider a system of two half-cells, each containing equal concentrations of NaCl. If a small amount of the  $\text{Na}^+$  in one of the half-cells is replaced by an equal amount of a radioisotope of a different element, say  $^{42}\text{K}^+$ , and the two half-cells are connected, the diffusion of the  $^{42}\text{K}^+$  may be traced [Figure 1(b)]. In this case, the diffusion of  $^{42}\text{K}^+$  is termed *tracer diffusion* to distinguish it from self-diffusion. At infinite dilution, the tracer diffusion and self-diffusion coefficients are the same.

Salt diffusion is illustrated in Figure 1(c). In this case, one half-cell contains a sodium chloride solution, whereas the other half-cell contains only the solvent. When diffusion is allowed, both the  $\text{Na}^+$  and the  $\text{Cl}^-$  diffuse in the same direction.

Counter-diffusion or interdiffusion describes the process whereby different ions are diffusing against, or in opposite directions to, each other. A system describing such a process is shown in Figure 1(d). In this system, two half-cells with equal concentrations of sodium chloride and potassium chloride are joined together, resulting in the diffusion of  $\text{Na}^+$  and  $\text{K}^+$  ions in opposite directions. This same process applies to any system in which concentration gradients are established in opposite directions. In reality, both self- and tracer diffusion are limiting cases of counterdiffusion, and salt diffusion and counterdiffusion usually occur simultaneously in most systems.

#### Fick's First Law

In free solutions (i.e., no porous matrix) diffusion is described mathematically by Fick's first law (9,10):

$$J_D = -D^0 \text{grad } c \quad (1)$$

where

$J_D$  = the diffusive mass flux, or the rate of transport of chemical species per unit cross-sectional area ( $\text{ML}^{-2}\text{T}^{-1}$ ),

$D^0$  = the free-solution diffusion coefficient of the chemical species ( $\text{L}^2\text{T}^{-1}$ ),

$c$  = the concentration of chemical species ( $\text{ML}^{-3}$ ), and

$\text{grad}$  = the gradient or vector differential operator ( $\text{L}^{-1}$ ).

The units of measurement used here are generic;  $M$  stands for mass,  $L$  stands for length, and  $T$  stands for time. The negative sign indicates that diffusion occurs in the direction of decreasing concentration. The following points can be made about Equation 1: (a) in general, the mass flux is a vector quantity (in bold type), (b) the equation applies to steady-state transport, and (c) the free-solution diffusion coefficient is assumed to be constant, which is a valid assumption only for relatively dilute solutions. If diffusion is assumed to occur in one direction, say the  $x$ -direction, then Equation 1 can be reduced to

$$J_D = -D^0 \frac{\partial c}{\partial x} \quad (2)$$

The diffusive mass flux has been changed from a vector to a scalar, because the direction of transport has been fixed.

#### Fundamental Basis for Diffusive Transport

There is a more fundamental basis for diffusive transport than Fick's first law, which is empirical. The fundamental basis results in a number of expressions that help to provide insight into some of the factors affecting the free-solution diffusion coefficient.

Under ideal conditions (i.e., microscopic scale, infinite dilution), the absolute mobility of a particle may be defined as the limiting velocity attained under a unit force (9). On the basis of the postulates of irreversible thermodynamics, the driving force for ions or molecules can be taken as the gradient in chemical potential or the partial molar Gibbs free energy of the chemical species. The combination of these relations, together with the definition of mass flux, results in an expression for diffusion known as the Nernst-Einstein equation (11):

$$J_D = \frac{uRT}{N} \frac{\partial c}{\partial x} \quad (3)$$

A comparison of Equations 1 and 3 reveals that the free-solution diffusion coefficient,  $D^0$ , is given by

$$D^0 = \frac{uRT}{N} \quad (4)$$

$$= ukT \quad (5)$$

where

$R$  = the universal gas constant ( $8.134 \text{ J mole}^{-1} \text{ K}^{-1}$ ),

$T$  = absolute temperature (in kelvins),

$N$  = Avogadro's number ( $6.022 \times 10^{23} \text{ mole}^{-1}$ ),

$u$  = the absolute mobility of the particle ( $\text{LT}^{-1}\text{F}^{-1}$ ), and

$k$  = Boltzman's constant ( $R/N$ ).

Equations 4 and 5 indicate that  $D^0$  is directly dependent on the absolute temperature of the solution.

Either Equation 4 or 5 can be combined with expressions

TABLE 1 SELF-DIFFUSION COEFFICIENTS FOR REPRESENTATIVE IONS AT INFINITE DILUTION IN WATER AT 25°C

Anion	$D^0 \times 10^{10} \text{ m}^2/\text{s}$	Cation	$D^0 \times 10^{10} \text{ m}^2/\text{s}$
OH <sup>-</sup>	52.8	H <sup>+</sup>	93.1
F <sup>-</sup>	14.7	Li <sup>+</sup>	10.3
Cl <sup>-</sup>	20.3	Na <sup>+</sup>	13.3
Br <sup>-</sup>	20.8	K <sup>+</sup>	19.6
I <sup>-</sup>	20.4	Rb <sup>+</sup>	20.7
HCO <sub>3</sub> <sup>-</sup>	11.8	Cs <sup>+</sup>	20.5
(a)NO <sub>3</sub> <sup>-</sup>	19.0	Be <sup>2+</sup>	5.98
SO <sub>4</sub> <sup>2-</sup>	10.6	Mg <sup>2+</sup>	7.05
CO <sub>3</sub> <sup>2-</sup>	9.22	Ca <sup>2+</sup>	7.92
		Sr <sup>2+</sup>	7.90
		Ba <sup>2+</sup>	8.46
		Pb <sup>2+</sup>	9.25
		Cu <sup>2+</sup>	7.13
		(a)Fe <sup>2+</sup>	7.19
		(a)Cd <sup>2+</sup>	7.17
		Zn <sup>2+</sup>	7.02
		(a)Ni <sup>2+</sup>	6.79
		(a)Fe <sup>3+</sup>	6.07
		(a)Cr <sup>3+</sup>	5.94
		(a)Al <sup>3+</sup>	5.95

(a) Values from reference (13)

relating the absolute mobility to the limiting ionic equivalent conductivity (9) and the viscous resistance of the solvent molecules, i.e., Stokes' law (12), to form two additional expressions for  $D^0$ , or:

$$D^0 = \frac{RT\lambda^0}{F^2|z|} \quad (6)$$

and

$$D^0 = \frac{RT}{6\pi N\eta r} \quad (7)$$

where

$F$  = the Faraday (96,490 coulombs),

$|z|$  = the equivalents, or charge, per mole of chemical species,

$\lambda^0$  = the limiting ionic equivalent conductivity (LT equivalent<sup>-1</sup>),

$\eta$  = the absolute viscosity of the medium (ML<sup>-1</sup>T<sup>-1</sup>), and

$r$  = the hydrated radius of the ion or molecule (L).

Equations 6 and 7 are referred to as the Nernst and the Einstein-Stokes equations, respectively. Although Equations 3 through 7 are of limited practical value, they do indicate that the free-solution diffusion coefficient is a function of the temperature and viscosity of the solution as well as the ionic valence and radius of the diffusing chemical species.

The Nernst equation can be used to calculate self-diffusion coefficients,  $D^0$ , provided the associated  $\lambda^0$  values are known (9). These calculations have been performed for a number of ions, and several representative  $D^0$  values are indicated in Table 1. Similar tables are provided elsewhere (13-16).

The values for  $D^0$  reported in Table 1 should be considered to be the maximum values attainable under ideal conditions. Under nonideal conditions (macroscopic scale, concentrated solutions), several effects, negligible for ideal conditions, become important. For convenience, the effects associated with nonideal diffusion can be separated into three groups: (a) those due to the requirements for electroneutrality, (b) those due to concentrated, nondilute solutions or electrolytes, and (c) those due to solution speciation or electrolyte strength.

### Effect of Electroneutrality

When two oppositely charged ions are diffusing in the same direction in solution (salt diffusion), a microscopic charge separation or electrical potential gradient is established between the ions because of their different mobilities. The effect of this charge separation is to speed up the slower-moving ion and to slow down the faster-moving ion. Because, on a macroscopic scale, electroneutrality must be satisfied, the resultant speeds of both ions must be equal (9).

As a result, each ion of an electrolytic solution is moving under the influence of not only the force due to the gradient in the chemical potential for that ionic species but also the force due to the gradient in the electrical potential between the motion of the oppositely charged particles. The end result is that the expressions for the free-solution diffusion coefficients of ions,  $D^0$ , must be modified to account for the additional force. This modification has been made for the specialized case of a single electrolyte, one molecule of which gives  $\nu_1$  cations of algebraic valency  $z_1$  and  $\nu_2$  anions of algebraic valency  $z_2$  (9). The theoretical development for this specialized case results in the following forms for the Nernst-Einstein expression (Equations 8a and 8b) and for the Nernst expression (Equations 9 and 10):

$$D_{12}^0 = \frac{u_1 u_2 (\nu_1 + \nu_2)}{\nu_1 u_2 + \nu_2 u_1} \left( \frac{RT}{N} \right) \quad (8a)$$

$$= \frac{D_1^0 D_2^0 (\nu_1 + \nu_2)}{\nu_1 u_2 + \nu_2 u_1} \quad (8b)$$

$$D_{12}^0 = \frac{\lambda_1^0 \lambda_2^0 (\nu_1 + \nu_2)}{(\lambda_1^0 + \lambda_2^0) \nu_1 |z_1|} \left( \frac{RT}{F^2} \right) \\ = \frac{\lambda_1^0 \lambda_2^0 (\nu_1 + \nu_2)}{(\lambda_1^0 + \lambda_2^0) \nu_2 |z_2|} \left( \frac{RT}{F^2} \right) \quad (9)$$

$$D_{12}^0 = \frac{\lambda_1^0 \lambda_2^0 (|z_1| + |z_2|)}{(\lambda_1^0 + \lambda_2^0) |z_1 z_2|} \left( \frac{RT}{F^2} \right) \quad (10)$$

where

$D_{12}^0$  = free-solution diffusion coefficient of the single electrolyte diffusing in one direction at infinite dilution ( $L^2 T^{-1}$ ),

$D_1^0$  and  $D_2^0$  = respective self-diffusion or tracer diffusion coefficients of the cation and the anion at infinite dilution, and

$\lambda_1^0$  and  $\lambda_2^0$  = respective limiting ionic conductances.

An expression for simple electrolyte diffusion similar in form to the Einstein-Stokes expression (Equation 7) is not valid, because Stokes' law applies only to individual particles or molecules.

Another equation similar in form to Equation 8 has been reported for the case where two different ions with the same valence and concentration gradient are diffusing in opposite directions, that is, counterdiffusion (11,14,17):

$$D_{12}^0 = \frac{(c_1 + c_2) D_1^0 D_2^0}{D_1^0 c_1 + D_2^0 c_2} \quad (11)$$

If the two ions have different valences, Equation 11 is modified as follows (13,18,19):

$$D_{12}^0 = \frac{(|z_1| n_1 + |z_2| n_2) D_1^0 D_2^0}{|z_1| n_1 D_1^0 + |z_2| n_2 D_2^0} \quad (12)$$

where  $n_1$  and  $n_2$  are the concentrations of the respective ions expressed as normalities (i.e., equivalents per liter of solution). In the cases described by Equations 11 and 12, the free-solution diffusion coefficient is the interdiffusion or counterdiffusion coefficient. It is interesting to note that the interdiffusion coefficient is controlled by the diffusion coefficient of the ion that is in the lower concentration. This unusual result can be seen by assuming  $c_1 \gg c_2$  in Equation 11 or  $n_1 \gg n_2$  in Equation 12, or vice versa.

General equations can be derived but not necessarily solved for cases where more than two ions are present because there is an infinite number of ways to satisfy the electroneutrality condition in such cases (9). Nevertheless, the above equations can be used to indicate the general effect of the electroneutrality condition. For example, Robinson and Stokes (9) have calculated the limiting free-solution diffusion coefficients for several simple electrolytes, and some of their results are reported in Table 2. A comparison of each of these limiting free-solution diffusion coefficients with their respective component self-diffusion coefficients given in Table 1 indicates the effect of the electroneutrality condition on the individual mobility of ions (i.e., in each case, the value for the limiting free-solution diffusion coefficient is between the values for each of its component self-diffusion coefficients).

### Effects of Concentration

As the concentration of the chemical species increases, solute-solute and solute-solvent interactions become more significant. The effects of the interactions on the free-solution diffusion coefficient are a function of the temperature and properties of the solvent (dielectric constant and viscosity), as well as the ionic strength of the solution (9,20). The overall effect is that the free-solution diffusion coefficient is a function of concentration. This concentration dependence for simple electrolytes is shown in Table 3, from which it is seen that there is no general trend of diffusion coefficient with concentration, and the difference in diffusion coefficients over a relatively broad range in concentrations is small.

### Effects of Speciation or Electrolyte Strength

Electrolytes can be classified into two broad categories (9): (a) nonassociated, completely dissociated, or strong electrolytes and (b) associated, incompletely dissociated, or weak electrolytes. The strong electrolytes consist of solutes existing only in the form of simple ions (i.e., cations and anions) possibly solvated. The weak electrolytes consist of solutes that can exist as associated (covalent) molecules as well as simple ions or ion pairs (complex species), or both, in which ion association occurs solely as a result of electrostatic attraction between oppositely charged ions. Thus far, the discussion of nonideal effects has pertained to nonassociated or strong electrolytes. There are two effects on the free-solution diffusion coefficient due to ion association (9): (a) the activity and therefore chemical potential of the solute is lower relative to that of a fully dissociated electrolyte, and (b) the resistance

TABLE 2 LIMITING FREE-SOLUTION DIFFUSION COEFFICIENTS FOR REPRESENTATIVE SIMPLE ELECTROLYTES AT 25°C (9)

Electrolyte	$D_{12}^0 \times 10^{10} \text{ m}^2/\text{s}$
HCl	33.36
HBr	34.00
LiCl	13.66
LiBr	13.77
NaCl	16.10
NaBr	16.25
NaI	16.14
KCl	19.93
KBr	20.16
KI	19.99
CsCl	20.44
CaCl <sub>2</sub>	13.35
BaCl <sub>2</sub>	13.85

TABLE 3 FREE-SOLUTION DIFFUSION COEFFICIENTS OF SELECTED CONCENTRATED AQUEOUS ELECTROLYTE SOLUTIONS AT 25°C (9)

Concentration (moles/liter)	$D_{12} \times 10^{10} \text{ m}^2/\text{s}$								
	NaCl	NaBr	NaI	KCl	KBr	KI	CaCl <sub>2</sub>	HCl	HBr
0.05	1.507	1.53	1.52	1.864	1.89	1.89	1.121	3.07	3.15
0.1	1.483	1.51	1.52	1.844	1.87	1.86	1.110	3.05	3.14
0.2	1.475	1.50	1.53	1.838	1.87	1.85	1.107	3.06	3.19
0.3	1.475	1.51	1.54	1.838	1.87	1.88	1.116	3.09	3.24
0.5	1.474	1.54	1.58	1.850	1.88	1.95	1.140	3.18	3.38
0.7	1.475	1.56	1.61	1.866	1.91	2.00	1.168	3.28	3.55
1.0	1.484	1.59	1.66	1.892	1.97	2.06	1.203	3.43	3.87
1.5	1.495	1.62	1.75	1.943	2.06	2.16	1.263	3.74	ND
2.0	1.516	1.66	1.84	1.999	2.13	2.25	1.307	4.04	ND
2.5	ND	1.70	1.92	2.057	2.19	2.34	1.306	4.33	ND
3.0	1.565	ND	1.99	2.112	2.28	2.44	1.265	4.65	ND
3.5	ND	ND	ND	2.160	2.35	2.53	1.195	4.92	ND
4.0	1.594	ND	ND	2.196 <sup>(a)</sup>	2.43	ND	ND	5.17	ND

(a) concentration = 3.19 moles/liter

ND=No Data

to the motion of two combined particles is less than that of the two particles when separated. Robinson and Stokes (9) have introduced an additional factor related to the degree of dissociation to account for these effects, and reference is made to their discussion for further details. The important point is that the strength of the electrolyte theoretically can affect the value for the free-solution diffusion coefficient.

### Effect of Pressure

Changes in pressure also can affect the value of the free-solution diffusion coefficient. The effect of pressure is realized primarily through changes in the viscosity of the solution and in the chemical potential of the solute. However, when water is the solvent, the pressure dependence of the diffusion coefficient is small (14). In most cases, the pressure dependence of the diffusion coefficient can be neglected.

### Fick's Second Law

When Fick's first law (Equation 1) is combined with the conservation of mass, the result is Fick's second law (9,10):

$$\frac{\partial c}{\partial t} = \text{div} (D^0 \text{grad } c) \quad (13)$$

where **div** is the divergence operator and  $t$  is time. The above equation applies to transient diffusion of an ionic species at infinite dilution in three-dimensional space. For diffusion in one direction (e.g., the  $x$  direction), Equation 13 becomes

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D^0 \frac{\partial c}{\partial x} \right) \quad (14)$$

If the free-solution diffusion coefficient is assumed to be independent of the distance of transport, Equation 14 can be reduced further to

$$\frac{\partial c}{\partial t} = D^0 \frac{\partial^2 c}{\partial x^2} \quad (15)$$

In general, Equations 14 and 15 are the forms of Fick's second law that are used in the study of the transient diffusion of solute species in free solutions.

### DIFFUSION IN SOIL

Diffusion in soil necessarily is slower than diffusion in free solution for three reasons (18):

1. There is a reduced cross-sectional area of flow,
2. There is a more tortuous diffusion pathway because of the particulate nature of the porous medium, and
3. There may be reduced mobility of the diffusing chemical species in the soil pores because of interactions with the pore walls.

The effects of reasons 1 and 2 are shown schematically in Figure 2. The effects of reason 3 are usually associated with adsorption-desorption reactions, although other chemical and biochemical reactions, as well as radioactive decay, may affect the mobility of chemical species diffusing in soil. Several modifications must be made to the free-solution diffusion equa-

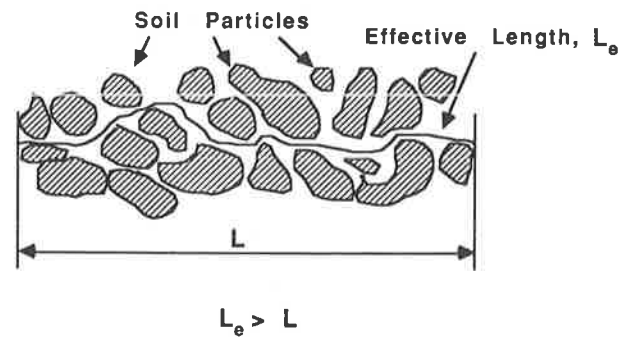


FIGURE 2 Concept of effective length in porous media.

tions (Fick's first and second laws) to account for the effects of soil on the diffusion of chemical species. In the following section, the modifications required to adapt Fick's laws to describe diffusion of contaminants in soil are covered. Diffusion in the gas phase of soil will not be covered in this paper.

### Effect of Reduction in Cross-Sectional Area of Flow

Under steady-state conditions when the concentration distribution is a linear function of distance, the differential operators in Equation 2 may be replaced by difference operators, or

$$J_D = -D^0 \frac{\Delta c}{\Delta x} \quad (16)$$

Because of the reduced cross-sectional area in the soil, the concentration of the diffusing species,  $c$ , is the concentration in the liquid phase of the pore space. Because fluxes are defined with respect to the total cross-sectional area, Equation 16 must be modified for diffusion in soil as follows:

$$J_D = -D^0 \theta \frac{\Delta c}{\Delta x} \quad (17)$$

where  $\theta$  is the volumetric water content defined as the volume of liquid per total volume of soil (dimensionless). Further, the volumetric water content may be defined as

$$\theta = nS_r \quad (18)$$

where  $n$  is the total porosity, or volume of voids per total volume of soil (dimensionless), and  $S_r$  is the degree of saturation, or volume of liquid per void volume, expressed as a decimal. When Equation 18 is substituted into Equation 17, Fick's first law for diffusion in soil becomes

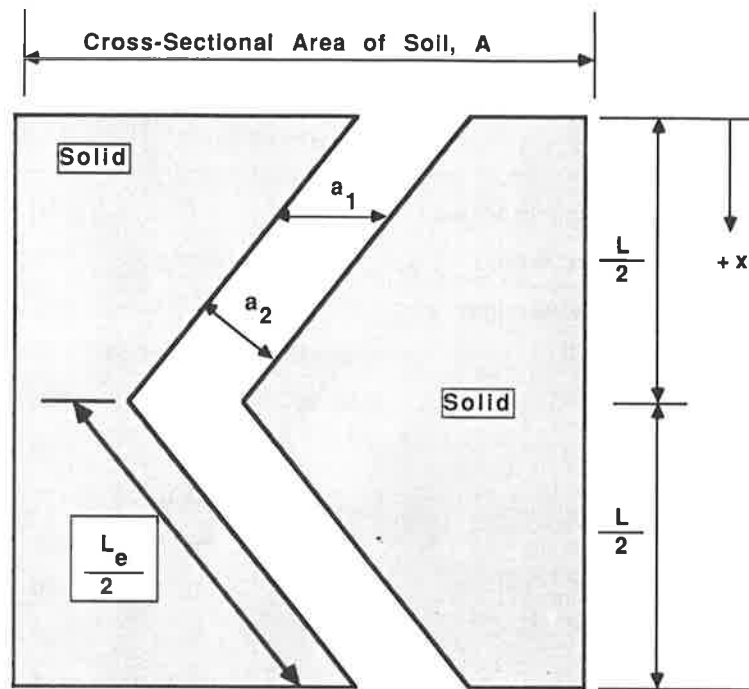
$$J_D = -D^0 n S_r \frac{\Delta c}{\Delta x} \quad (19)$$

Therefore, the most conservative case (i.e., maximum flux for liquid phase diffusion) will occur when the soil is saturated ( $S_r = 1.0$ ), all other conditions being equal.

### Effect of Tortuous Pathway

There are two effects due to the more tortuous pathway associated with diffusion through soils:

1. The cross-sectional area perpendicular to the actual,



$$\begin{aligned}
 n &= \frac{a_1}{A} & \Delta x &= L = x_2 - x_1 \\
 a_2 &= \left(\frac{L}{L_e}\right) a_1 & \Delta x' &= L_e \\
 n' &= \frac{a_2}{A} = \left(\frac{L}{L_e}\right) n & \frac{\Delta x'}{L_e} &= \frac{\Delta x}{L} \\
 & & \frac{\Delta c}{\Delta x'} &= \frac{\Delta c}{\left(\frac{L}{L_e}\right) \Delta x} = \left(\frac{L}{L_e}\right) \frac{\Delta c}{\Delta x}
 \end{aligned}$$

where

$A, a_1, a_2$  = areas  
 $L, L_e, \Delta x, \Delta x'$  = lengths

FIGURE 3 Schematic representation illustrating the effects on diffusion due to tortuous nature of pathway [after Porter et al. (23)].

microscopic flow direction in the soil is less than that perpendicular to the macroscopic flow direction defined by the  $x$  coordinate system, and

2. The driving force (i.e., concentration gradient) is also less because of the longer, or actual, length of flow,  $L_e$ , versus the macroscopically measured length of flow,  $L$  (21-23).

Each of these effects is illustrated schematically for a saturated system in Figure 3.

As a result of these effects, Equation 19 must be modified to describe the process of diffusion in soil, as follows:

$$J_D = -D^0 n' S_r \frac{\Delta c}{\Delta x'} \quad (20)$$

where  $n'$  and  $\Delta x'$  are the actual (microscopic) porosity and distance of flow, respectively. Because macroscopic quantities are desired for the measurement of diffusion coefficients, the macroscopic equivalents for  $n'$  and  $\Delta x'$  may be substituted into Equation 20 (see Figure 3):

$$J_D = -D^0 \left(\frac{L}{L_e}\right) n S_r \frac{\Delta c}{\left(\frac{L_e}{L}\right) \Delta x} \quad (21a)$$

$$= -D^0 \left(\frac{L}{L_e}\right)^2 n S_r \frac{\Delta c}{\Delta x} \quad (21b)$$

The factor  $(L/L_e)^2$  is purely geometric and is defined as the tortuosity of the porous medium (21-23). Since  $L < L_e$  for porous media,  $(L/L_e)^2 < 1.0$ . The tortuosity factor is usually represented by  $\tau$ :

$$\tau = (L/L_e)^2 \quad (22)$$

When Equations 18, 21, and 22 are combined, Fick's first law for diffusion in soil becomes

$$J_D = -D^0 \tau \theta \frac{\Delta c}{\Delta x} \quad (23)$$

### Effective Diffusion Coefficient

At present, tortuosity factors cannot be measured independently. This obstacle is surmounted by defining an effective diffusion coefficient,  $D^*$ , where

$$D^* = D^0 \tau \quad (24)$$

TABLE 4 REPRESENTATIVE TORTUOSITY FACTORS TAKEN FROM THE LITERATURE

Tracer(s)	Soil(s)	Saturated or Unsaturated	$\tau$ Values <sup>(a)</sup>	Reference
<sup>36</sup> Cl	50% Sand:Bentonite Mixture	Saturated	0.08-0.12	(24)
	Bentonite:Sand Mixtures	"	0.04-0.49	(25)
	Bentonite:Sand Mixtures	"	0.59-0.84	(26)
	Silt Loam	Unsaturated	*0.05-0.55	(27)
	Sand	Saturated	*0.28	(28)
	Loam	"	*0.36	(28)
	Clay	"	*0.31	(28)
Cl <sup>-</sup>	Clayey Till	"	*0.15	(2)
	Silty Clay	"	*0.13-0.30	(4)
	Silty Clay	"	*0.10	(6)
	Sandy Loam	Unsaturated	*0.21-0.35	(29)
	Silty Clay Loam;Sandy Loam	Saturated	*0.08-0.22	(30)
	Kaolinite	"	*0.12-0.50	(31)
	Smectitic Clay	"	*0.07-0.24	(31)
Cl <sup>-</sup> & SO <sub>4</sub> <sup>2-</sup>	Clay	"	0.55	(13)
Br <sup>-</sup>	Silty Clay Loam;Sandy Loam	"	*0.19-0.30	(30)
	Kaolinite	"	*0.15-0.42	(31)
	Smectitic Clay	"	*0.08	(31)
	Sandy Loam	"	*0.25-0.35	(32)
<sup>3</sup> H	Bentonite:Sand Mixtures	"	0.01-0.22	(25)
	Bentonite:Sand Mixtures	"	0.33-0.70	(26)

(a) Values with \* were calculated using appropriate  $D^0$  value from Table 1 with the  $D^*$  value taken from the reference.

When Equation 24 is substituted into Equation 23, Fick's first law for diffusion in soil becomes

$$J_D = -D^* \theta \frac{\partial c}{\partial x} \quad (25)$$

where the difference operators in Equation 23 have been replaced by the differential operators to denote generality. Since  $\tau < 1.0$ ,  $D^* < D^0$  and diffusion in soil is slower than diffusion in free solution. Equation 25 can be used to measure effective diffusion coefficients of chemical species,  $D^*$ , diffusing in soil. Following the measurement of  $D^*$ , the tortuosity factor can be determined through Equation 24, using an appropriate value for the free-solution diffusion coefficient. The appropriate free-solution diffusion coefficient to be used depends on the type of diffusion coefficient being measured (i.e., self, tracer, counterdiffusion, or salt) and the system employed to measure it (i.e., infinite dilution or not,

single, simple, or multiple electrolyte solution). However, in most cases, the free-solution diffusion coefficient for a single solute species at infinite dilution ( $D^0$ ) has been used to determine  $\tau$ -values, as indicated by Equation 24. Some typical values for  $\tau$  reported in the literature are presented in Table 4. (As noted in Table 4, some of the  $\tau$ -values are based on the results of diffusion tests performed with unsaturated soils.)

#### Fick's Second Law

The transient form of the transport equation for diffusion in soil depends on whether the chemical species, or tracer, is nonreactive or reactive. A chemical species is nonreactive if it is not subject to chemical reactions, biological transformations, and radioactive decay (33). A reactive chemical species is subject to chemical and biochemical reactions or radioactive decay, or both.



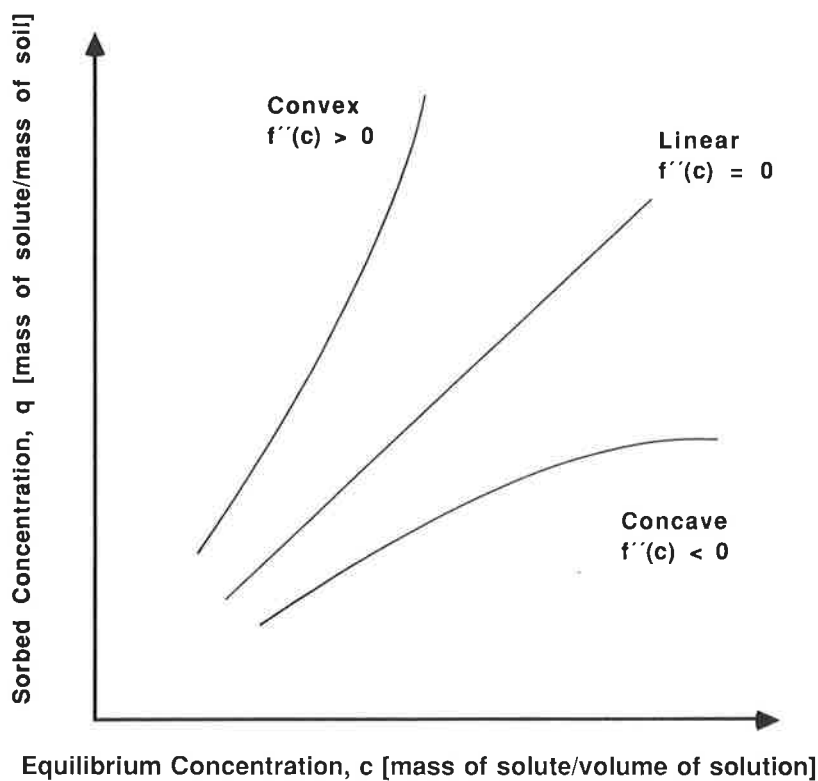


FIGURE 4 General shapes for adsorption isotherms [ $f''(c)$  denotes second derivative].

When Fick's first law (Equation 25) is combined with the equation of continuity (i.e., conservation of mass), the result is Fick's second law for the transient diffusion of a nonreactive chemical species in soil (21,33):

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D^* \frac{\partial c}{\partial x} \right) \quad (26)$$

or, if  $D^*$  is not a function of the transport distance,

$$\frac{\partial c}{\partial t} = D^* \frac{\partial^2 c}{\partial x^2} \quad (27)$$

Excellent discussions of the types of chemical and biological reactions affecting inorganic chemicals are provided elsewhere (33–36).

Of the numerous types of chemical or biochemical reactions that can affect contaminant concentrations during transport in soil, only adsorption-desorption (sorption) reactions are routinely modeled. The other reactions typically are accounted for by indirect, qualitative analyses. For reactive solutes subject to reversible sorption reactions during diffusive transport in soil, Equation 27 must be modified as follows:

$$\frac{\partial c}{\partial t} = \frac{D^*}{R_d} \frac{\partial^2 c}{\partial x^2} \quad (28)$$

where the retardation factor,  $R_d$ , is given by the following equation:

$$R_d = 1 + \frac{\rho_b}{\theta} K_p \quad (29)$$

where  $\rho_b$  is the dry (bulk) density of the soil ( $\text{ML}^{-3}$ ) and  $K_p$  is the partition coefficient ( $\text{L}^3\text{M}^{-1}$ ). The partition coefficient relates the mass of solute sorbed per mass of soil,  $q$ , to the

concentration of the solute in solution,  $c$ , at equilibrium. The relationship between  $q$  and  $c$ , known as an adsorption isotherm, is often determined for an appropriate range of concentrations from the results of batch equilibrium tests. Three general shapes for adsorption isotherms resulting from batch-equilibrium tests are shown in Figure 4. When the  $q$  versus  $c$  relationship is constant, the adsorption isotherm is linear ( $f''(c) = 0$ ), and  $K_p$  is termed the *distribution coefficient*,  $K_d$ . Otherwise,  $K_p$  is a function of the equilibrium concentration in soil [i.e.,  $K_p = f(c)$ ]. Since the effective diffusion coefficient in Equation 28 is divided by the retardation factor, the rate of diffusive transport of a chemical species undergoing reversible sorption reactions is inversely proportional to the value of the partition coefficient.

When the adsorption isotherm is nonlinear, the resulting differential equation describing solute transport in soil with simultaneous adsorption (Equation 28) is nonlinear, for which no general analytical solutions exist. However, analytical solutions do exist when the adsorption behavior is linear. The existence of analytical solutions makes the assumption of linear adsorption desirable. For this reason, linear adsorption isotherms are often assumed to apply when, in fact, experimental data suggest nonlinear adsorption behavior.

#### Apparent Diffusion Coefficients

Some researchers have found it convenient to rewrite Equation 28 as follows:

$$\frac{\partial c}{\partial t} = D_A^* \frac{\partial^2 c}{\partial x^2} \quad (30)$$

where  $D_A^*$  is an apparent diffusion coefficient (13), also known

as the effective diffusion coefficient of the reactive solute,  $D_s$  (15,26), or

$$D_A^* = D_s = \frac{\bar{D}^*}{R_d} \quad (31)$$

The result of this substitution is that only one unknown ( $D_A^*$  or  $D_s$ ) must be solved for, instead of two unknowns ( $D^*$ , and  $R_d$  or  $K_p$ ). Then, based on some information regarding either  $D^*$  or  $K_p$ , and the known value of  $D_A^*$ , the other unknown parameter may be solved for by Equation 31.

However, Rowe et al. (37) and Rowe (38) caution against the use of a single coefficient,  $D_A^*$  or  $D_s$ , in Equation 28 when the boundary conditions are flux-controlled, since the resulting analyses will be both incorrect and unconservative. In addition, the coefficient  $D_A^*$  or  $D_s$  is a function of the sorption characteristics of the soil, whereas  $D^*$  is not. Therefore, it is meaningless to report a value for  $D_A^*$  or  $D_s$  without reporting the associated  $R_d$  value, since different soils have different sorption characteristics.

## DIFFUSION THROUGH SOIL BARRIERS

### Transport Mechanisms

Three transport mechanisms—advection, mechanical dispersion, and molecular diffusion—are generally recognized as governing the flow of contaminants in porous materials. Advection is the transport of contaminants in response to a gradient in total hydraulic head. Due to advection, nonreactive contaminants are transported at an average rate equal to the seepage velocity,  $v_s$  ( $LT^{-1}$ ), which, for a saturated system, is defined as

$$v_s = \frac{v}{n} = \frac{ki}{n} \quad (32)$$

where

- $v$  = the Darcian velocity ( $LT^{-1}$ ),
- $k$  = the hydraulic conductivity or permeability of the soil ( $LT^{-1}$ ), and
- $i$  = the hydraulic gradient (dimensionless).

Both mechanical dispersion and molecular diffusion are mixing processes that cause the contaminant front to spread out or disperse during transport through the porous material. However, mechanical dispersion is a function of the seepage velocity, whereas molecular diffusion is not (i.e., the greater the seepage velocity, the greater the effect of mechanical dispersion, and vice versa). Therefore, even though all three mechanisms are active during transport, the effect of mechanical dispersion becomes less significant as the seepage velocity decreases. For the relatively low seepage velocities typically associated with fine-grained soil barriers, the effect of mechanical dispersion is negligible (38). As a result, the transport of contaminants through waste containment barriers generally can be described using an appropriate advective-diffusive model.

The appropriate model to be used depends on the susceptibility of the contaminant to geochemical reactions (i.e., nonreactive versus reactive solutes) and the overall flow conditions. In general, three possible cases should be considered (see Figure 5): (a) diffusion without advection (pure diffu-

sion), (b) diffusion with positive advection, and (c) diffusion with negative advection. Each case is discussed in the following sections.

### Diffusion Without Advection

For the case shown in Figure 5a, the hydraulic gradient across the clay barrier is zero, so there is no advective flow. However, because the concentration of the contaminants in the leachate is greater than that in the natural soil, a concentration gradient is established across the barrier. As a result of this concentration gradient, diffusion of contaminants will occur through the barrier. The appropriate equations for modelling this case have been presented previously. Under steady-state conditions, the diffusive flux of contaminants is described by Equation 25. The transient diffusive transport of contaminants can be modelled by using Equation 27 for the nonreactive solutes and Equation 28 for the reactive solutes.

The significance of pure diffusive transport of contaminants across clay barriers can be illustrated with the aid of an example. If the concentration of contaminants in the leachate is assumed to be constant with time, then the concentration of the contaminant reaching the bottom of a clay barrier of thickness  $L$  can be described as a function of time, using the following analytical solution to Equation 27 (10):

$$\frac{c}{c_0} = \operatorname{erfc} \left[ \frac{L}{2(D^*t)^{1/2}} \right] \quad (33)$$

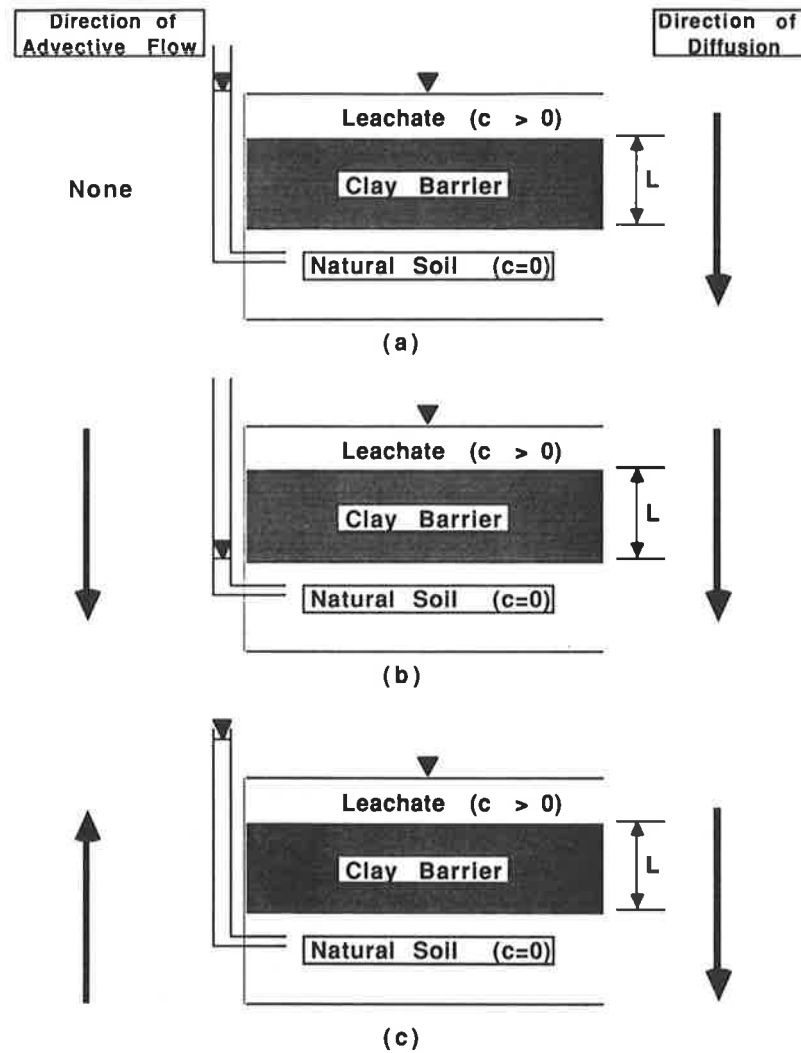
where

- $c_0$  = the concentration of the nonreactive solute in the leachate,
- $c$  = the corresponding concentration at the bottom of the barrier,
- $\operatorname{erfc}(\ )$  = the complementary error function, and
- $t$  = the transit time (i.e., the time required for the solute to travel from the top to the bottom of the barrier).

Tables of values for the  $\operatorname{erfc}(\ )$  are given by Abramowitz and Stegun (40), Carslaw and Jaeger (39), Crank (10), and Freeze and Cherry (33), among others. A reasonable estimate for the effective diffusion coefficient ( $D^*$ ) of a nonreactive solute, such as chloride ( $Cl^-$ ), is  $6.0 \times 10^{-10}$   $m^2/sec$  (8,31). Based on this  $D^*$  value, the relative concentrations,  $c/c_0$ , at the bottom of the clay barrier have been plotted in Figure 6 for a 50-year period as a function of the barrier thickness. Since, in many cases, these values for  $c/c_0$  represent concentrations that may exceed allowable standards, it is apparent that diffusion through fine-grained soil barriers can be a significant transport process, especially for relatively thin barriers. Since the boundary conditions upon which Equation 33 is based are not flux-controlled, a similar analysis could be performed for reactive solutes by substituting  $D_A^*$  or  $D_s$  for  $D^*$  in Equation 33.

### Diffusion with Positive Advection

For the case shown in Figure 5(b), a hydraulic gradient has been established across the clay barrier such that advective flow of contaminants occurs in the same direction as the dif-



**FIGURE 5** Flow conditions for waste containment barriers: (a) diffusion without advection (pure diffusion), (b) diffusion with positive advection, and (c) diffusion with negative advection.

fusives flow in the pure diffusive case. The advective flow is termed *positive* because it results in an increase in the contaminant concentration in the natural soil. This case is commonly described in texts on contaminant transport (21,33,41). For this case, the total, steady-state flux,  $J$ , of the contaminant is given by the sum of the advective flux,  $J_A$ , and the diffusive flux,  $J_D$ , or

$$J = J_A + J_D \tag{34}$$

where

$$J_A = nv_s c \tag{35}$$

and  $v_s$  is given by Equation 32. Since  $J_D$  is given by Equation 25, the total flux (assuming saturated conditions) is described by

$$J = nv_s c - D^* n \frac{\partial c}{\partial x} \tag{36}$$

The transient model for this case, assuming a homogeneous soil, is described by the well-known advective-dispersive equation for nonreactive solutes (21,33,41):

$$\frac{\partial c}{\partial t} = D^* \frac{\partial^2 c}{\partial x^2} - v_s \frac{\partial c}{\partial x} \tag{37}$$

where mechanical dispersion has been considered to be negligible. There are several analytical solutions to Equation 37, depending on the boundary and initial conditions (21,41). One of the more popular solutions is as follows (33,42,43):

$$\frac{c}{c_0} = \frac{1}{2} \left\{ \operatorname{erfc} \left[ \frac{x - v_s t}{2(D^* t)^{1/2}} \right] + \exp \left( \frac{xv_s}{D^*} \right) \operatorname{erfc} \left[ \frac{x + v_s t}{2(D^* t)^{1/2}} \right] \right\} \tag{38}$$

Equation 38 applies to a semiinfinite medium in which the concentration of the contaminant in the leachate,  $c_0$ , is assumed to be constant with time.

As previously indicated, the transport of contaminants through clay barriers is a function of the magnitude of the seepage velocity. An example of this dependence is illustrated in Figure 7 where the transit times for several relative concentrations ( $c/c_0$ ) have been plotted versus the seepage veloc-

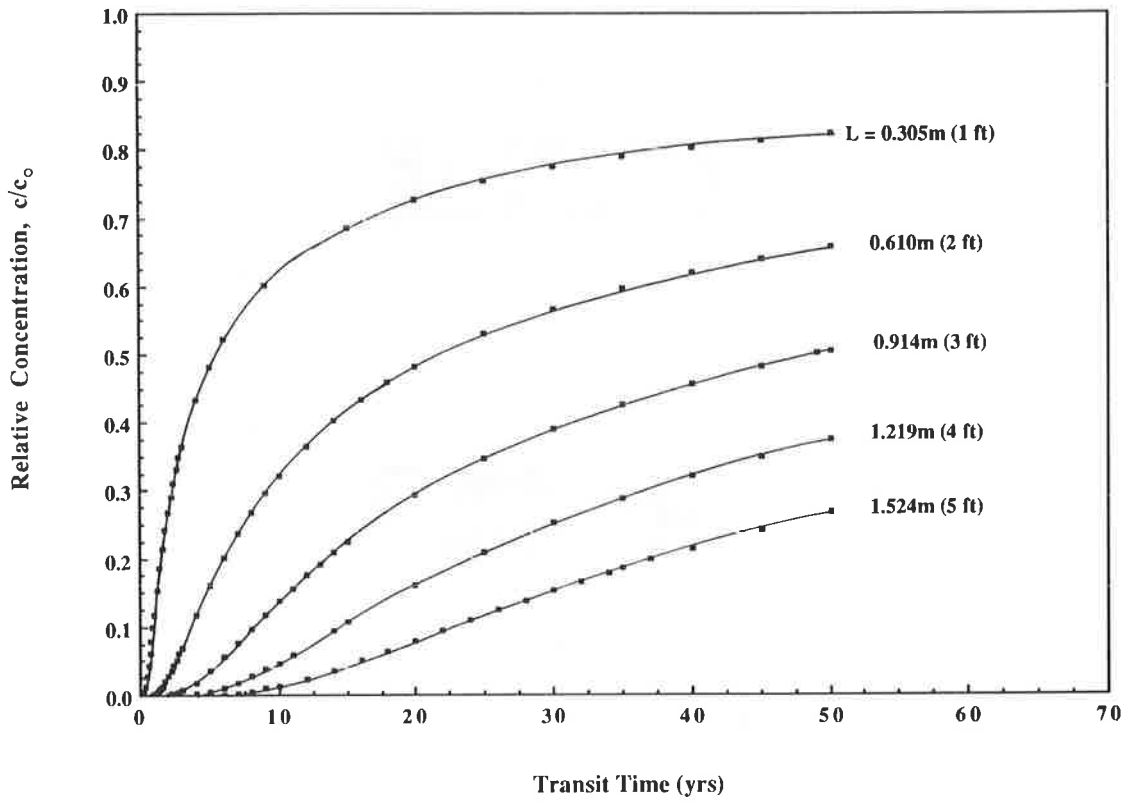


FIGURE 6 Relative concentration ( $c/c_0$ ) versus transit time due to pure diffusive transport.

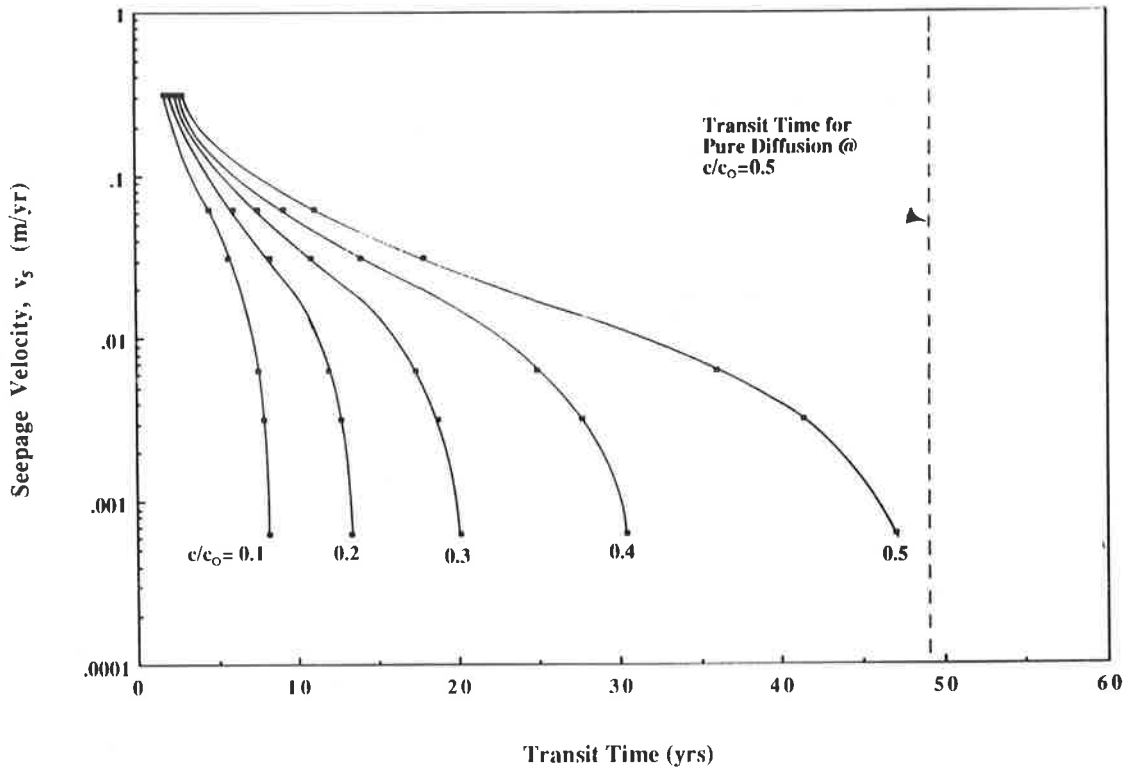


FIGURE 7 Effect of seepage velocity on contaminant transit times due to diffusion with positive advection [data for  $L = 0.914\text{ m}$  (3 ft)].

ity. The data for Figure 7 were generated using Equation 38 for the case where  $D^*$  equals  $6.0 \times 10^{-10}$  m<sup>2</sup>/sec and  $x$  ( $= L$ ) is 0.914 m (3 ft). The data presented in Figure 7 indicate that, as the seepage velocity decreases, the transit time approaches asymptotically a limiting value that is based on pure diffusive transport. In the limit, when the seepage velocity approaches zero, the analytical solution for the advective-diffusive transport (Equation 38) reduces to the analytical solution for pure diffusive transport (Equation 37). Therefore, the transit times based on pure diffusive transport given in Figure 6 represent the limiting values for the case of diffusion with positive advection.

For example, the transit time based on pure diffusive transport for a barrier thickness of 0.914 m (3 ft) and a relative concentration of 0.5 is approximately 49 years (see Figure 6). This value is represented in Figure 7 by a vertical line, which indicates the independence of diffusion on the seepage velocity. As a result, the best containment barrier that can be built for the case of positive advection is one in which diffusion is the controlling mechanism of contaminant transport. However, relatively short transit times may still result even though diffusion is the controlling mechanism of transport, especially for relatively thin barriers and/or low values of  $c/c_0$  (see Figures 6 and 7).

For reactive solutes subject to reversible sorption reactions, Equation 37 is not an appropriate model. Instead, Equation 37 must be modified as follows:

$$\frac{\partial c}{\partial t} = \frac{D^*}{R_d} \frac{\partial^2 c}{\partial x^2} - \frac{v_s}{R_d} \frac{\partial c}{\partial x} \quad (39)$$

Equation 38 also represents an analytical solution to Equation 39 if  $D^*$  in Equation 38 is replaced by  $D^*/R_d$ .

### Diffusion with Negative Advection

In some instances, the direction of advective transport may be opposite that of diffusive transport, as shown in Figure 5(c). This situation may occur in practice, for example, when the barrier (either natural or man-made) is located over a confined aquifer under artesian pressure, or when vertical barriers, such as slurry walls, are used to isolate a contaminated area (see Figure 8). In this case, the advective flow is termed *negative* because it works to prevent the escape of pollutants from the contaminated area.

The steady-state and transient equations describing this case can be formulated by simply substituting  $-\nu_s$  for  $\nu_s$  in the equations for the previous case (i.e., Equations 36, 37, and 39). However, the boundary and flow conditions for this case can be quite complex. For example, if the concentration,  $c_2$ , in the slurry wall scenario in Figure 8 is initially zero, then there is no initial advective flux of contaminants into the barrier. The initial flow of water into the containment area may dilute the concentration  $c_1$  with time and, therefore, reduce the concentration gradient for outward (positive) diffusive transport. The contaminant migration front, if any, will depend on the offsetting effects of the advective and diffusive fluxes. The situation for reactive solutes is more complex. Regardless, significant diffusive transport of contaminants may still result if a relatively thin barrier is built to contain high concentrations of priority pollutants over extended periods.

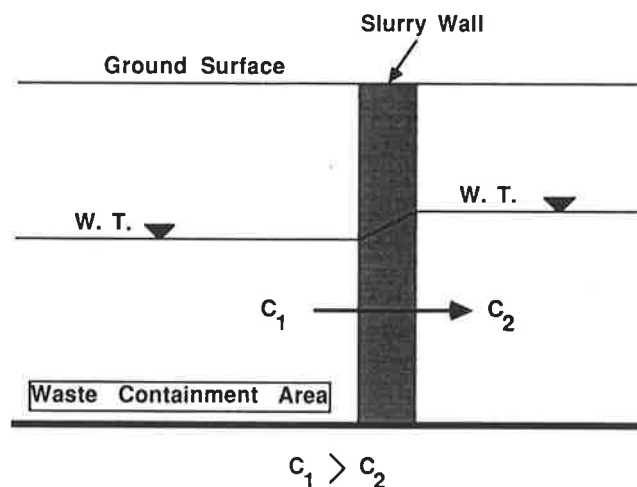


FIGURE 8 Slurry wall scenario for case of diffusion with negative advection.

### SUMMARY AND CONCLUSIONS

The steady-state diffusion of solutes (ions, molecules) in free solutions is described by Fick's first law. This law, which is empirical, is supported by several more fundamental expressions (e.g., the Nernst-Einstein, Nernst, and Einstein-Stokes equations). These expressions, derived for ideal conditions (microscopic scale, infinite dilution), must be modified for non-ideal conditions. The more fundamental expressions provide insight into the factors affecting the free-solution diffusion coefficient. The major factors include the temperature, viscosity, and dielectric constant of the solution; the radius and valence of the diffusing chemical species; and the equilibrium chemistry of the solution (i.e., the requirement for electroneutrality, speciation or electrolyte strength, and concentration of the solute).

Solutes diffusing in soil are subject to a more reduced cross-sectional area of flow, a greater distance of flow, and more tortuous pathways than are solutes in free solutions. As a result, diffusion in soil is slower than diffusion in free solution. In addition, some solutes may experience a reduced mobility in the soil due to adsorption reactions with the soil particles. Due to these effects, Fick's first and second laws for diffusion in free solution must be modified in order to describe the steady-state and transient diffusion, respectively, of solutes in soil. The modifications required are described in this paper.

Diffusion of contaminants through fine-grained soil barriers is a significant, if not dominant, transport mechanism. The significance of diffusion to the overall migration of contaminants increases as the seepage velocity decreases. Even if the seepage velocity is zero, release rates of contaminants by diffusion can be high, especially when relatively high concentrations of contaminants are being contained by relatively thin barriers. As a result, severe consequences can result if diffusive transport of contaminants is not considered in the design of waste containment barriers.

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