

## Diffusion in Saturated Clayey Barrier Medium

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### Abstract

The design of clay/clayey barriers for the containment of buried wastes conventionally has been based on the assumption that the hydraulic conductivity controls the rate of leachate percolation. However, recent studies show that diffusion is a controlling mechanism of solute transport in many fine-grained soils. Although the measurement of the hydraulic conductivity of fine-grained soils is comparatively a common practice in soil engineering, the measurement of diffusion coefficients is not. As such, it is becoming increasingly essential to assess the movement of chemicals through soil barriers due to diffusion. Studies indicate that diffusion may be an important, if not dominant mechanism of contaminant transport through waste containment barriers. This paper is therefore in line with the efforts made in the measurement of diffusion coefficients of inorganic chemicals passing through saturated soils. Herein, both steady-state and transient equations relating to the diffusive transport of inorganic chemicals are presented. A number of factors affecting diffusion coefficients are identified and a simple method for measuring diffusion coefficients for a compacted barrier is defined. The definition for the diffusion coefficient of soil called the effective diffusion coefficient,  $D^*$  is seen to vary widely. Generally, the variations are due to the different factors affecting diffusion of solutes in soil and the various ways of including the volumetric water content in the governing equations. Hence, errors in interpretation and comparison of  $D^*$  values can occur if the appropriate definition is not used. In a nutshell, the concept of diffusion may be unfamiliar to many soil specialists, worsened by the myriad terminologies linked to the study of diffusion in soils. Thus the study attempts to acquaint soil engineers with vital information for the measurement of diffusion coefficients for barrier designs.

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### 1. Introduction

Usually the design of soil barriers for waste containment purposes has over the years relied on the supposition that hydraulic conductivity controls leachate percolation rate. On the contrary, studies by [1-6] have shown diffusion to be the dominant and controlling mechanism of solute migration in many fine-grained soils. Hence, it is insistently crucial to assess the transport of contaminant species through clay/clayey barriers due to diffusion. The evaluation of the hydraulic conductivity of fine-grained soils is comparatively a common practice in soil engineering. However, the assessment of diffusion coefficients has generally never been of paramount concern so soil experts over past decades. More to this, many soil engineers may be unaccustomed to the concept of diffusion in fine-grained soils

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and as such, fail to recognize its dominance as a controlling mechanism in the transportation process of solute through soils. Furthermore, there are wide variations in literature on the terminology associated with the study of diffusion in soils. These varying terminologies cause significant misperception and requires massive amounts of time to narrow out essential details. This paper is therefore in line with efforts and attempts made to describe the phenomenon of diffusion in soils. Although the main aim of this work is to acquaint soil engineers with the basic information necessary for the measurement and assessment of diffusion coefficients incorporated into the design of barriers for waste containment. Thus, equations needed to describe diffusion of solutes in soil are presented, factors influencing diffusion coefficients are also briefly discussed as well as some light shed on the measurement approaches, and the variability in the terminologies linked to the study of diffusion in soils.

### Nomenclature

Percolation	a process whereby a liquid slowly passes through barrier or media
Diffusion	the random movement of particles due to kinetic energy occurring in a gaseous or liquid medium
Leachate	liquid that drains from a landfill containing both dissolved and suspended solids

## 2. Steady/Quasi Steady-State Diffusion

### 2.1. Diffusion in Free Solution

The diffusion of a chemical or contaminant species in a solute is usually presumed to arise in reaction to a concentration gradient in accordance with Fick's first law which, for one dimension, may be expressed as shown in Equation (1).

$$J = -D_o \frac{\partial c}{\partial x} \quad (1)$$

In Equation (1)  $J$ ,  $c$ ,  $x$  and  $D_o$ , are; the mass flux, the concentration of the solute in the liquid phase, the direction of transport and the free solution diffusion coefficient, respectively. Nevertheless, older studies by a number of authors [7-9] have noted the existence of a more central basis for diffusive transport other than the empirical Fick's first law. According to the authors, this basis takes the driving force for the solute ions as the gradient in the chemical potential of the contaminant species, resulting in a number of expressions one of which is the Nernst-Einstein by [10] represented by Equation (2), offering insight into the factors influencing the free solution diffusion coefficient,  $D_o$ . On comparison with Equation (1), the expression for the free solution diffusion coefficient at infinite dilution i.e., whereby due to adequate dilution the solute ions do not interact while in solution, giving rise to Equation (3).

$$J = - \frac{\mu RT}{N} \frac{\partial c}{\partial x} \quad (2)$$

$$D_o = - \frac{\mu RT}{N} \quad (3)$$

In Equation (3)  $R$ ,  $T$ ,  $N$  and  $\mu$ , are; the universal gas constant (8.134 J/mol/K), the absolute temperature, Avogadro's number ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ) and the absolute mobility of a particle, respectively. As recorded by [11] the absolute mobility of a particle is the limiting velocity reached under a unit force which, in the abovementioned case, is the gradient in the chemical potential of the diffusing contaminant species. Combining Equation (3) with expressions connecting the absolute mobility to the limiting ionic equivalent conductivity and to the viscous resistance of the solvent molecules, i.e., Stokes Law, two additional expressions for  $D_o$  is derived as shown in Equations (4) and (5).

$$D_o = \frac{RT \lambda_o}{F^2 |z|} \quad (4)$$

$$D_o = \frac{RT}{6 \pi N \eta r} \quad (5)$$

In Equations (4) and (5)  $F$ ,  $|z|$ ,  $\lambda_o$ ,  $\eta$  and  $r$ , are; the Faraday (96,490 Coulombs/equivalent), the absolute value of the ionic valence, the limiting ionic conductivity, the absolute viscosity of the solution and the molecular or hydrated ionic radius, respectively. As recorded by [12] the limiting ionic conductivity is the conductivity of an aqueous solution containing the specified ion at infinite dilution. The Equations (4) and (5) commonly are known as the

Nernst and the Einstein-Stokes equations, respectively, and show that  $D_o$  is influenced by several factors, including the temperature and viscosity of the solution, and the radius and valence of the diffusing contaminant species [12].

### 3. Diffusion Types

The value of  $D_o$  relies on the diffusion type. An older study detailed by [12] recorded essentially four diffusion types: (1) self-diffusion (2) tracer-diffusion (3) salt-diffusion, and (4) inter-diffusion/counter-diffusion. A schematic representation of these diffusion types are illustrated in Fig. 1. Here, the diffusion compounds are assumed to be sodium chloride (NaCl) and/or potassium chloride (KCl). In self-diffusion, the initial system would contain two half-cells of equal concentrations of NaCl, but without any isotopically different species. In this system, the movement of the molecules would be random, but the motion of the molecules would not be traced. As such, the self-diffusion system is estimated by the addition of the isotopic (tracer) species, as shown in Fig. 1a. In this case, each half-cell of the system initially contains an equal concentration of NaCl. Although in one half-cell, a small amount of  $\text{Na}^+$ , is substituted by its isotope,  $^{22}\text{Na}^+$ . When the two half-cells are linked, diffusion of both  $\text{Na}^+$  and its isotope,  $^{22}\text{Na}^+$ , occurs, but in opposite directions, due to the small concentration gradients of each species. Since the concentration gradient is particularly 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 signs i.e.,  $\text{Cl}^-$ , and the tracer ions may be considered to be moving relative to a stationary background of non-diffusing ions [12].

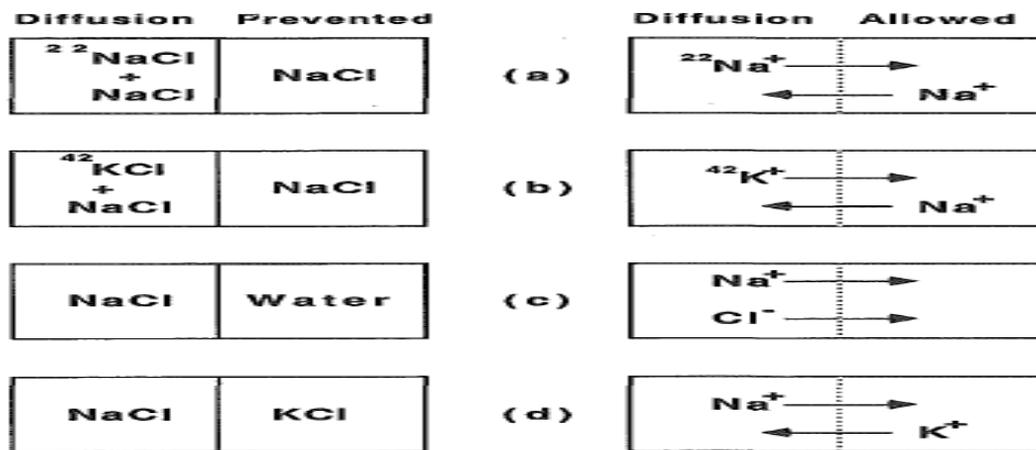


Fig. 1. Diffusion cells for different systems: (a) self-diffusion (b) tracer diffusion (c) salt diffusion, and (d) interdiffusion [12]

This movement of the tracer ions is termed self-diffusion, and the diffusion coefficient describing it is called the self-diffusion coefficient. Tracer-diffusion is identical to self-diffusion except the isotopic species is of a different element. For instance, consider a system of two half-cells, each containing equal concentrations of NaCl, if a small amount of  $\text{Na}^+$  in one of the half-cells is substituted by an equal amount of a radioisotope of a different element, say  $^{42}\text{K}^+$ , and the two half-cells are linked, the diffusion of the  $^{42}\text{K}^+$  may be traced as depicted in Fig. 1b. In this case, the diffusion of  $^{42}\text{K}^+$  is termed tracer-diffusion to differentiate it from self-diffusion. At infinite dilution, the tracer-diffusion and self-diffusion coefficients are identical. Whereas in the case of salt-diffusion as shown in Fig. 1c, one half-cell contains a NaCl solution while the other half-cell contains only the solvent. When diffusion occurs, both the  $\text{Na}^+$  and the  $\text{Cl}^-$  ions diffuse in the same direction. The inter-diffusion defines the process involving different ions diffusing against or in opposite directions, illustrated in Fig. 1d. Here, two half-cells with equal concentrations of NaCl and KCl are fused, leading to diffusion of  $\text{Na}^+$  and  $\text{K}^+$  ions in opposite directions. This process applies to any system in which concentration gradients are in opposite directions. Equations for inter-diffusion coefficients have been recorded by [7, 8, 10]. In actual sense, both self- and tracer-diffusion are limiting cases of inter-diffusion whilst salt- and inter-diffusion occur simultaneously in most systems. However, the best scenario yet, representing the most practical field condition in the use of natural soil barriers in waste containment is depicted in Fig. 1c.

#### 4. Diffusion in Soil

Solutes diffuse at slower rates in soil than in free solution plausibly due to the more tortuous pathways for migration in soil. Moreover, diffusive mass fluxes are less in soil than in free solution because solid particles in soil occupy some of the cross-sectional area. These effects are shown in Fig. 2.

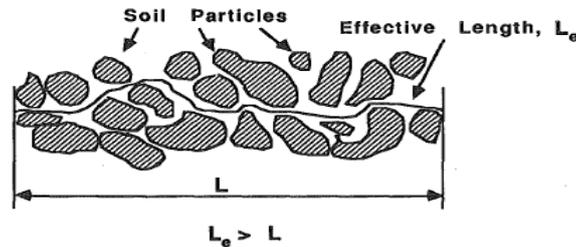


Fig. 2. Conceptualized representation of effective length in transport through soil [12]

##### 4.1. Influence of Reduction in Cross-Sectional Area of Flow

Due to the reduced cross-sectional area of flow in soil, the concentration of the diffusing species,  $c$ , is the concentration in the liquid phase of the pore space as noted by [12]. Since fluxes are defined with respect to the total cross-sectional area, Equation (1) becomes modified for diffusion in soil as expressed by Equation (6).

$$J = -D_o \theta \frac{\partial c}{\partial x} \quad (6)$$

Where;  $\theta$  is the volumetric water content expressed by Equation (7).

$$\theta = nS_r \quad (7)$$

In Equation (7)  $n$  and  $S_r$  are; the total soil porosity and the degree of saturation of the soil, expressed as a decimal. Hence, the maximum flux for liquid phase diffusion will occur when the soil is saturated ( $S_r = 1.0$ ) and all other conditions in Equation (6) unchanged.

##### 4.2. Influence of Tortuous Pathway of the Soil

The tortuosity of the soil as reported by [12] is often accounted for by adding into Equation (6) a tortuosity factor,  $\tau$ , thus resulting in Equation (7).

$$J = -D_o \tau \theta \frac{\partial c}{\partial x} \quad (8)$$

##### 4.3. Other Influences

There are additional influencing factors that tend to reduce the rate of diffusive transport of solutes in soil. Incorporating the fluidity or mobility factor,  $\alpha$ , accounts for the increased viscosity of the water adjacent to the clay mineral surfaces relative to that of the bulk water. More to this, a factor,  $\gamma$ , accounts for exclusion of anions from the smaller pores of the soil. Anion exclusion can result in compacted clays and shales when clay particles are pressed closer together such that the diffuse double layer of ions associated with the particles occupies much of the remaining pore space. The process is also known as salt filtering, ultrafiltration or membrane filtration. Anion exclusion may occur in natural deposits when the average porosity of the soil has been reduced to 0.3. This may also be operative in highly unsaturated soils and in relatively small pores where the available cross-sectional area of flow is reduced. Thus Equation (8) becomes modified to cater for the additional influencing factors in Equation (9).

$$J = -D_o \tau \alpha \gamma \theta \frac{\partial c}{\partial x} \quad (9)$$

Considering that in most cases it is difficult, if not impossible, to separate the effects of geometry ( $\tau$ ), fluidity ( $\alpha$ ) and anion exclusion ( $\gamma$ ) in soil diffusion studies, it seems best to define a single factor that accounts for all of them. Thus, it has been done by defining the impedance factor,  $f_i$ , which is further discussed in future studies.

## 5. Effective Diffusion Coefficient

Presently, tortuosity factors cannot be measured independently and as such, becomes suitable to define an effective diffusion coefficient,  $D^*$ , as expressed by Equation (10).

$$D^* = D_0 \tau \quad (10)$$

Substituting Equation (10) into (8), the Fickian first law for diffusion in soil becomes expressed as Equation (11).

$$J = -D^* \theta \frac{\partial c}{\partial x} \quad (11)$$

From Equation (11) effective diffusion coefficients of contaminant species,  $D^*$ , diffusing in soil from experimental results can be determined. After which the apparent tortuosity factor,  $\tau$ , can be calculated using Equation (10) with a fitting value for the free-solution diffusion coefficient. There are several definitions for  $D^*$ , besides that of Equation (10). Care must be taken when interpreting  $D^*$  of various researchers as errors in interpretation of 50% or more can occur if inappropriately defined [12].

## 6. Definition of Concentration

Several authors as recorded by [12] have defined solute concentration in terms of the total volume of soil i.e.,  $c' = \theta c$ , and have modified and rewritten Equation (11) into (12) in terms of concentration.

$$J = -D^* \frac{\partial c'}{\partial x} \quad (12)$$

Where the definition of  $D^*$  involves volumetric water content i.e.,  $D^* = D_0 \tau \theta$ , Equation (12) becomes Equation (13).

$$J = -D_{\theta}^* \frac{\partial c'}{\partial x} \quad (13)$$

And where;

$$D_{\theta}^* = \frac{D^*}{\theta} \quad (14)$$

## 7. Transient Diffusion

### 7.1. Nonreactive Solutes

The Fickian first law defines steady/quasi-steady state diffusive flux of solutes. For transient (time-dependent) transport of nonreactive solutes in soil, Fick's second law is assumed to take effect, or where  $D^*$  applies, and expressed by Equation (15).

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

### 7.2. Reactive Solutes

The transport of contaminant species not subject to chemical and/or biochemical reactions are known as nonreactive solutes. Whereas, transported solutes that are subject to chemical and/or biochemical reactions, are called reactive solutes, and they differ significantly from the transport of nonreactive solutes. Out of the several types of chemical and/or biochemical reactions that can influence contaminant concentrations during transport in soil, only adsorption desorption (sorption) reactions and radioactive decay are usually modeled. Whereas dissolution, precipitation, oxidation-reduction, and ion pairing or complexation reactions are usually not modeled.

For non-decaying, reactive solutes subject to reversible sorption reactions during diffusive transport in soil, Equation (15) becomes (16).

$$\frac{\partial c}{\partial t} = D^* \frac{\partial^2 c}{\partial x^2} - \frac{\partial q'}{\partial t} \quad (16)$$

Where  $q'$  is the sorbed concentration of the contaminant species expressed in terms of the mass of sorbed species per unit volume of voids i.e., occupied by the liquid phase, or where  $q$  is the sorbed concentration expressed as the mass of solute sorbed per mass of soil and  $\rho_d$  is the dry (bulk) density of the soil.

On differentiating Equation (16) with respect to time, substituting it into Equation (15) and the resulting expression rearranged, Fick's second law for reactive solutes subject to reversible sorption reactions during diffusive transport in soil is gotten. However, this will be covered in further works together with adsorption isotherms, apparent diffusion coefficients and influence of coupled flow processes.

## 8. Measuring Approaches

A number of methods reported by [12, 13] have been initiated in the measurement of  $D^*$ . One of many practices is to saturate two half-cells of soil with different solutions, place the half-cells together and allow diffusion to occur. Subsequently, the apparatus is disassembled, the soil is sectioned to determine the resulting concentration profile within the sectioned soil profiles, and the experimental outcomes results are curve-fit with an analytical solution to Equation (15) or other equations not addressed herein to determine the  $D^*$ . Conversely, this method may be unsuitable for compacted clayey/fine-grained soils plausibly due to the difficulty in obtaining good contact between the half-cells, inter-diffusion may also exist when the interest often is in salt diffusion, and it is comparatively problematic to saturate low-permeability soils in the two half-cells with leachate [12]. However, a more appropriate practice for measuring  $D^*$  in compacted clayey soils is based on the techniques described by [14-16]. This concept illustrates how soil is compacted in a mold, soaked to destroy suction that might produce advective mass transport and then the soil is exposed to leachate in a reservoir. The difference in concentration of solutes establishes a concentration gradient between the reservoir and the compacted soil and the concentration of solutes in the reservoir decreases with time. This concept will be further discussed under the influence of coupled flow processes in future works. At the end of the diffusion test, the soil is extruded and sectioned, and the aqueous phase of each section is analyzed to develop a profile of solute concentrations within the soil. The  $D^*$  for a nonreactive solute or the ratio  $D^*/R_d$  for a reactive solute is calculated from the variation in solute concentration in the reservoir versus time and/or from the profile of solute concentrations in the soil at the end of the test. Where  $R_d$  is the retardation factor for associated sorption characteristic of the soil [12].

## 9. Conclusion

The paper has attempted to describe the equations used for the diffusive transport of inorganic contaminants in free-solutions and in soils. The empirical Fickian first law was used to describe the diffusion in aqueous or free solution. A number of central expressions for Fick's first law was used to shed light on the factors influencing the free-solution diffusion coefficient ( $D_0$ ). A few influencing factors are the temperature and viscosity of the solution, the radius and valence of the diffusing contaminant species, and solute-solute and solute-solvent interactions. Furthermore, the value for  $D_0$  relies on the measurement system initiated. Four different diffusion systems were briefly discussed and it was indicated that the diffusive transport in soil is slower than diffusive transport in free solution because of the reduced cross-sectional area of flow and the more tortuous pathways experienced by solutes diffusing through soil. Additionally, solutes may be subject to adsorption reactions that further decreases their migration rate. It has long be established that the definition for  $D^*$ , for diffusion in soil varies widely due to a various factors but most importantly due to the volumetric water content,  $\theta$ , and caution should be exercised in interpreting or comparing the outcomes to measure  $D^*$  of various researchers as errors could occur if wrongly defined. It is suggested that all factors that influence  $D^*$  of nonreactive solutes be combined into a single factor called the apparent tortuosity factor,  $\tau$ , and considering that the  $\theta$ , is an independently determined variable, it should not be included in the definition of the effective diffusion coefficient,  $D^*$ . Even though further reporting is required, the effective diffusion coefficients can be measured in cells in which compacted soils are saturated and equilibrated

to eliminate suction that would cause mass transport through advection and then exposed to a reservoir of leachate after which sectioning can be done to determine the distribution profile of diffusing solutes at the end of the test. Finally, the  $D^*$  can be determined either from the rate reduction in solute concentration or from the final solute concentration in the sectioned soil profiles.

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