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Diffusion of Inorganic Contaminants

In Dense Clay

Wihel Al-Tai

A Thesis

in

The Department

of

Civil Engineering

Presented in Partial Fulfillment of the Requirements

for the Degree of Master of Applied Science at

Concordia University

Montreal, Quebec, Canada

January 1994

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ABSTRACT

Diffusion of Inorganic Contaminants In Dense Clay

Wihel Al-Tai

To assess the safety of the waste disposal site, a knowledge of the molecular diffusion coefficients through the liner is required. The methods commonly used in the laboratory to determine these coefficients are very time consuming. Because of the large number of species, the changing environmental factors, the different clay types generally encountered in the field, and the long time required to determine the diffusion coefficient, it is not feasible to cover the whole range of diffusion coefficients required. Hence, developing a mathematical model that is capable to predict the diffusion coefficient based on simple parameters is needed. In this study, the diffusion mechanism in clay is presented and the diffusion parameters are analysed. A model that allows the diffusion coefficients to be predicted in dense clay is presented. The model showed that diffusion coefficient depends on the charge nature and size of the diffusing species, water chemistry, soil structure, and temperature. The predicted diffusion coefficients for some species are shown to be in good agreement with those measured in dense bentonite.
ACKNOWLEDGEMENTS

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List of Symbols

\( a \) activity

\( A \) area

\( \text{Å} \) angstrom.

\( \gamma \) activity coefficient

\( C \) concentration.

\( D \) diffusion coefficient

\( D_A, D_a \) transient-state diffusion coefficient.

\( D_A' \) steady-state diffusion coefficient

\( D_h \) hydrodynamic dispersion coefficient

\( D_o \) free-solution diffusion coefficient

\( D_p \) pore diffusion coefficient

\( f \) unit force

\( f_r \) frictional resistance

\( f_V \) viscosity factor

\( F \) Faraday.

\( F_d \) driving force

\( H \) double layer thickness

\( i \) hydraulic gradient

\( i_g \) gradient factor

\( J \) flux.
List of Symbols (cont'd)

k  Boltzman constant
K  hydraulic conductivity.
K_d distribution coefficient.
K_p partition coefficient.
m  mobility factor.
m_r mole fraction.
N  Avogadro's number.
r  radius.
R  retardation factor.
S  amount of sorbed species
S_r degree of saturation.
t  time.
T  temperature.
U  absolute mobility.
V  limiting velocity.
V_m average velocity.
X  distance.
Z  charge valance.
\( \alpha \) dispersivity.
List of Symbols (cont'd)

$\alpha_l$ longitudinal dispersivity.
$\alpha_t$ transverse dispersivity.
$\beta$ sliding frictional coefficient.
$\delta$ fraction of the water that is available for diffusion.
$\eta$ volumetric water content
$\mu$ viscosity.
$\lambda$ equivalent ionic conductivity.
$\gamma_{bulk}$ bulk density.
$\gamma_d$ clay density.
$\theta$ total porosity.
$\theta_e$ effective porosity.
$\theta_{ef}$ effective-free porosity.
$\theta_{es}$ effective-surface porosity.
$\tau$ tortuosity factor.
$\zeta$ dielectric constant.
$\epsilon$ unit electric charge.
$\Psi$ chemical potential.
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CHAPTER 1

Introduction

1.1 Problem

A major environmental problem facing the world these days is the intrusion of toxic and hazardous wastes from landfill disposal sites to the groundwater supply system and the surrounding environment. These wastes can be grouped under three main categories: (1) household wastes, (2) industrial wastes and (3) nuclear wastes.

The problem of contaminant migration has been known since ancient times, but the effect of this problem was not significantly noticed because the human population was low and dispersed. However, this problem now poses a serious threat to the quality of groundwater because of the recent industrial revolution and the big growth in human population. As a result, a number of methods have been utilized in an attempt to minimize contaminant migration. One of these methods is the use of clay liners. A clay liner, which is mainly composed of clay materials, is increasingly used as a sealant in the engineering design of waste disposal sites to limit and inhibit the migration of contaminants to the groundwater and the surrounding environment. A good example is the use of a compacted mixture of bentonite and sand to surround the waste containers in the disposal vaults for
the Canadian nuclear fuel waste (Cheung 1989). Figure 1.1 shows schematic view of a landfill site and a nuclear waste disposal site.

The problem of contaminant migration remains in our limited knowledge of where and how much contaminants will transport from the disposal site to the surrounding environment. Knowing how the contaminants migrate will enable us to make intelligent decisions about the disposal of these wastes and the remedial actions that should be taken if the waste is improperly disposed.

### 1.2 Need

Contaminant migration through the clay liner and the underlying material is a combination of the advection and the diffusion processes. The migration due to groundwater flow is termed as advection, whereas, the migration due to the difference in concentration, i.e. chemical potential, is termed as diffusion. Since clay material has a very low hydraulic conductivity ($<10^{-10}$ m/sec), the principle mechanism of mass transport through the liner and the underlying clay soil will be by the diffusion process. Therefore, the diffusion coefficients are critical parameters for predicting the migration rates and the fluxes through these materials.

Several methods have been developed and used to measure the diffusion coefficients. These values are found to vary by order of magnitude for the same species under the same conditions and when using different methods (Oscarson et al. 1992). The
Figure 1.1 schematic view of (a) landfill site  
(b) nuclear waste disposal vault
cause of these variations are due to our limited knowledge about soil structure and to the improper use of the terminology used in describing the diffusion coefficients. To explain the reasons for the discrepancies in these data a clear understanding of the diffusion process is needed. The diffusion coefficients are also found to depend on several factors, such as: type of diffusing species, clay density and type, and other environmental factors, like temperature, groundwater chemistry, density of the underlying material, etc. (Cheung 1989). Because of the large number of species, the changing environmental factors, the different clay types generally encountered in the field, and the long time required to determine the diffusion coefficient, it is not feasible to cover the whole range of diffusion coefficients required. Hence, developing a mathematical model that is capable to predict the diffusion coefficients based on simple parameters is needed.

A model based on free water in the soil has been developed and is referred to as the free-water model. This model has been used to predict the diffusion coefficients; it is found to be valid for sandy soil (Gillham et al. 1984), but not valid for clay (Cheung 1989). Therefore, a model that is suitable for clay soil is required.

1.3 Objectives

The objectives of this study are:

1) To provide a comprehensive understanding of the migration process and the terminology commonly used to describe the diffusion process.
2) To give a brief review of the different methodologies used to determine the diffusion coefficients and its application to field condition.

3) To improve the existing model to predict the diffusion coefficients for clay soils based on simple parameters.

4) To explain the discrepancy in the diffusion data obtained from the various methods.

1.4 Organization of the Thesis

The thesis is organized as follow:

- Introduction
- Literature Review
  - Migration Processes
  - Diffusion in Pure Liquid
  - Diffusion in Porous Media
  - Methodologies To Determine The Diffusion Coefficient
    - Free-Water Model
    - Clay-Water-Interaction Model
    - Parametric-Analysis And Relationship
- Conclusions And Recommendations
CHAPTER 2

Literature Review

2.1 Migration Processes

Landfill disposal sites are mainly designed to prevent waste components from being in contact with living things, in other words to prevent waste leakage. Since there isn't any facility that is totally free of leakage, the migration of contaminants is inevitable; it is therefore desirable that we have the ability to analyze how and where contaminants will migrate. In order to accomplish this, a general understanding of the migration processes is required. Waste migration can be described by the mass balance equation and it is expressed by the following (Freeze and Cherry, 1979):

\[
\text{Change in mass} = \text{Flux out} - \text{Flux in} \pm \text{Loss or Gain} \quad (2.1)
\]

of contaminants

in contaminants

The processes that control the flux in and flux out of an elemental volume are: advection and hydrodynamic dispersion. The loss or gain of contaminants in the volume can occur as a result of chemical, biochemical reactions, and/or radioactive decay. These processes are illustrated in Figure 2.1. Some of these processes are briefly introduced in the following sections.
Figure 2.1 Physical and chemical processes involved in contaminant migration
2.1.1 Advection Process

The advection process occurs when contaminants move through a medium as a result of groundwater flow. Species under this process will be transported at an average groundwater velocity \( V_m \). According to Darcy's law, the rate of transport can be calculated from (Craig 1987):

\[
V_m = \frac{K_i}{\Theta}
\]

where \( V_m \) = average velocity.

\( K \) = Hydraulic conductivity.

\( i \) = Hydraulic gradient.

\( \Theta \) = Porosity.

The above equation shows that groundwater velocity is directly related to both the hydraulic conductivity and the hydraulic gradient. Because of the very low hydraulic conductivity and the low hydraulic gradient of the clay soil commonly encountered in the field advection process is not likely to be the major mechanism.

2.1.2 Hydrodynamic Process

The hydrodynamic process occurs due to the mechanical mixing during fluid advection and results in the spreading of contaminants. Two processes contribute to the hydrodynamic process: (1) mechanical dispersion, which is advection dependent, and (2) diffusion, which is concentration dependent.
2.1.2.1 Mechanical Dispersion

Mechanical dispersion is a mixing process due to velocity variations within a porous medium. These variations are caused by the following reasons, see Figure 2.2, (Freeze and Cherry 1979):

(1) Variation due to the drag force exerted on the fluid by the size and roughness of the pore surface, i.e. the geometry of the pore.

(2) Variation due to the difference in viscosity of flowing fluid through a pore.

(3) Variation due to tortuosity, branching and interfinger ing of pore channel.

Mechanical dispersion is usually characterized by the term dispersivity and it is represented by the symbol $\alpha$, sometimes referred to as dynamic dispersivity. Dispersivity has two components:

$\alpha_L = \text{Longitudinal dispersivity in the direction of flowing fluid.}$

$\alpha_T = \text{Transverse dispersivity in the direction perpendicular to the direction of flowing fluid.}$

According to Freeze and Cherry (1979) longitudinal dispersion is normally much stronger than transverse dispersion.
Figure 2.2  Microscopic components of mechanical dispersion
(1) effect of pore size and roughness.
(2) effect of viscosity.
(3) effect of pathway.
2.1.2.2 Diffusion

Diffusion occurs due to the difference in contaminant concentration, which results in a net flux of contaminant toward the zone of lower concentration. According to Fick’s first law, diffusion of contaminant in one direction can be calculated from:

\[ J = -D \frac{\partial C}{\partial X} \]  \hspace{1cm} (2.3)

where \( J \) = Flux

\( D \) = Diffusion coefficient

\( C \) = Concentration

\( X \) = Distance

\( \frac{\partial C}{\partial X} \) = Concentration gradient

The usual practice in determining the hydrodynamic dispersion is by combining both mechanical dispersion and diffusion in one term, known as the hydrodynamic dispersion coefficient and defined as:

\[ D_H = \alpha V_m + D \]  \hspace{1cm} (2.4)

where \( D_H \) = Hydrodynamic dispersion coefficient.

\( \alpha \) = Dispersivity (longitudinal or transverse).

\( V_m \) = Darcian velocity.

\( D \) = Diffusion coefficient.
Since hydraulic conductivity and hydraulic gradient in compacted clay materials are very low, advection and mechanical dispersion processes are not likely to be the mechanisms by which contaminant will transport through compacted clay soil. As a result, contaminant movement through this type of soil will be dominated by the diffusion process. In order to better understand the diffusion process, the remainder contains a general and brief discussion of the mechanisms of diffusion and the retardation processes. This is followed by a detailed discussion about the diffusion of contaminants in both pure liquid and porous media.

2.1.3 Mechanism of Diffusion

One of the most interesting aspects of the diffusion process is the mechanism of this movement. Under diffusion mechanism, contaminants can be transported over a relatively large distance. What is desirable here is a clear picture of the trajectory of the species as they move through the media. In porous media contaminants will diffuse through both solids and liquids. The simplest type of this mechanism is shown in Figure 2.3; it mainly occurs in solid state. Figure 2.3(a) shows the first stage of the diffusion process, where a contaminant atom is surrounded by the host media atoms. The size of these atoms are small when compared to those of the host atoms. The movement of the contaminant through the host media is done by pushing some of the host atoms surrounding it and jumping into a new position near the original one. This process is illustrated in Figures 2.3(b) and Figure 2.3(c). In Figure 2.3(b) the contaminant atom is midway between the original and the final position, this is called the activated state. At this
stage, the contaminant atom encounters a strong repulsive force; therefore, a considerable amount of energy is required to enable the contaminant to push and pass its neighbors. The source of this energy is the thermal vibration of the atoms themselves. Figure 2.3(c) shows the contaminant atom in its new position after completing the jump. Since this mechanism requires high thermal energy, solid diffusion is not likely to occur in landfill disposal sites and it can be neglected. However, solid diffusion could be important in the fuel bundle in nuclear reactor, where large amount of thermal energy may generated.

Figure 2.3 (a) Contaminant atoms before an atomic jump.  
(b) Contaminant atoms in activated state.  
(c) Contaminant atoms after an atomic jump.
In pure liquid media the movement of atoms is called self-diffusion. Self-diffusion occurs by exchanging the position of atoms without changing the original structure. The simplest way in which self-diffusion can take place is by direct interchange between two adjacent atoms, as shown in Figure 2.4 (a). In Figure 2.4 (a), atom A moves to replace atom B position, and atom B replaces atom A position. This type of motion will cause large distortion to the surrounding atoms, therefore it is not likely to occur. There are other types of such mechanism, one of them is the ring mechanism in which a number of atoms moves simultaneously to replace each other position in a ring motion as shown in Figure 2.4 (b). In the four atoms ring mechanism, atom A moves to atom B position, atom B moves to atom C position, atom C moves to atom D position, and finally atom D moves to atom A position. While the local distortion caused by this mechanism is less than that in the direct mechanism, the ring mechanism requires a cooperative action where all members of the ring must move at once. This cooperative motion has a lower probability of occurrence than the direct interaction. Therefore, this type of diffusion mechanism

Figure 2.4 (a) Direct interaction mechanism for self-diffusion
(b) Four-ring mechanism for self-diffusion
depends on the balance between the energy required to overcome the repulsion force of the surrounding atoms while they are being displaced by the moving atoms and on the probability that the proper cooperative motion takes place. Theoretical calculation strongly suggested that the ring mechanism is favored over the direct interaction (Girifalco 1964).

There are other types of diffusion mechanisms that may occur for different systems, such as diffusion by interstitially mechanism and by vacancy mechanism. Since the aim of this study is to understand the diffusion process itself rather than understanding the mechanism of diffusion, detailed understanding of the diffusion mechanism is beyond the scope of this study.

2.1.4 Retardation Processes

A number of processes may occur in clay which can result in retardation of contaminant migration. These processes could be physical, chemical, and/or biological, see Figure 2.1. The physical and the biological processes are not within the scope of this study, hence, they are not discussed here.

In the chemical reaction process, more attention is given to the reactions between clay particles and contaminant species. Chemical reactions usually occur between the surface of the clay particles and the diffusing species; these reactions depends on: the composition of the clay materials, the type of the diffusing species and the distribution of
the species in the soil-solution media. Such interactions will usually be associated with two mechanisms (Dunn 1983): (1) adsorption-desorption, and (2) distribution of ions in the clay water system.

2.1.4.1 Adsorption-desorption

Adsorption-desorption in clay minerals is the result of two mechanisms: ion exchange, and adsorption process these processes are discussed below.

2.1.4.1.1 Ion-Exchange

Different clays have different charge deficiencies and thus have different tendencies in adsorbing certain anions and cations; these ions are retained in an exchangeable state. The exchangeable ions are held around the outer side of the clay unit cell and the exchange reaction does not affect the structure of the unit cell.

Cation Exchange

Clay particles usually carry a net negative charge on their surface which is mainly due to isomorphous substitution, broken bonds and the replacement of hydrogen of an exposed hydroxyl (Mitchell 1976). These negatively charged particles are balanced or neutralized by exchangeable cations attracted to their surface. These cations are termed exchangeable because one cation can be replaced by another cation of equal valance, or by two cations of one-half the valance of the original one. The quantity of exchangeable cations required to balance the charge deficiency of a clay is termed the cation exchange
capacity (CEC) and it is usually expressed in milliequivalents\(^1\) per 100 grams of dry clay. The range of cation exchange capacity of the commonly used clay minerals are listed in Table 2.1.

Cation exchange is a reversible process that is governed by two main properties: (1) the valence of the cation and (2) the size of the cation. The valence of the cation has the dominant influence: the higher the valence, the greater the replacing power or the harder to replace if the cation of higher valance is at the surface. For ions of the same valance, increasing cation size gives greater replacing power (Yong et al. 1966). A typical replaceability series of exchangeable cations is shown in Table 2.1.

Cation exchange is a diffusion process, i.e. it is a time-dependent mechanism and the rates vary between clay minerals. In kaolinite the exchange occurs instantaneously, whereas in illite and chlorite the exchange requires a few hours. In montmorillonite, a longer time is required because of its large specific surface area and the cations must diffuse between the mineral layers.

**Anion Exchange**

Although little is known about this process, anion exchange may occur in clay minerals. This is due to either the replacement of hydroxyl ions or the adsorption of ions with similar shapes to the edge of the silica tetrahedral sheet, such as phosphate (Dunn 1983). Some clay minerals, like kaolinite, at low pH level their edges are positively charged, thus anion exchange would be expected (Mitchell 1976).

---

\(^1\) Equivalent weight = atomic weight / valence.
Table 2.1

Cation Exchange Capacity of the commonly used clay minerals
(in milliequivalent per 100 grams)

<table>
<thead>
<tr>
<th>Clay Mineral</th>
<th>Range of CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>3 - 15</td>
</tr>
<tr>
<td>Illite</td>
<td>10 - 40</td>
</tr>
<tr>
<td>Chlorite</td>
<td>10 - 40</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>80 - 150</td>
</tr>
</tbody>
</table>

(after Grim 1962)

Typical Series

$\text{Na}^+ < \text{Li}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{Mg}^{+2} < \text{Ca}^{+2} < \text{Sr}^{+2} < \text{Ba}^{+2}$

$< \text{Cu}^{+2} < \text{Al}^{+3} < \text{Fe}^{+3} < \text{Th}^{+3}$

(after Mitchell 1976)
2.1.4.1.2 Adsorption Process

Adsorption quantitatively expresses the relation between the amount of species sorbed by clay particles and the equilibrium concentration of this species in a bulk liquid. Adsorption can be determined by performing batch-equilibrium tests in the laboratory. The tests are carried out by mixing a known amount of soil and chemical solution in a predetermined mixing ratio for a specific period of time at a constant temperature. The mixing ratio can be used as 1:4 soil to solution ratio by weight, and the mixing time is often ranged between 24 to 48 hours at room temperature 20°C to 25°C. The initial concentration of the chemical species is measured before the solution is added to the soil and the equilibrium concentration is measured after the mixing is completed. The amount of sorbed species is determined by taking the difference between the two measured concentrations. The above procedure is repeated several times with different initial solute concentrations in order to establish the relationship between the sorbed species and the equilibrium concentration. The resulting relationship is known as an adsorption isotherms, the term isotherms is used because the test is performed at a constant temperature.

The relationship between the sorbed species and the equilibrium concentration can be either linear or non-linear (concave up or concave down), as shown in Figure 2.5. Approximating the retardation factor by using non-linear adsorption isotherms are much more difficult to develop, therefore, linear adsorption isotherms are often used. The different types of adsorption isotherms and adsorption isotherms equations are discussed in more detail in the following sections.
Figure 2.5 Adsorption isotherms curves
(a) linear relation
(b) non-linear (concave up)
(c) non-linear (concave down)
2.1.4.1.2.1 Adsorption Isotherm Equations

Adsorption of contaminant species by clay particles occurs because of the various interaction forces that exist between the surface of the active clay particles and the contaminant species. These interactions play an important role in determining the type of adsorption isotherm relation. The classical typical set of adsorption isotherms are shown in Figure 2.6.

There are mainly two types of adsorption isotherms: linear and non-linear. The general equation used to define adsorption isotherms is expressed by the following relation (Yong et al. 1992):

\[ S = K_p C \]  \hspace{1cm} (2.5)

where \( S \) is the amount of contaminant species that has been sorbed by the clay particles per unit mass of the clay specimen, \( C \) is the equilibrium concentration and \( K_p \) is the partition coefficient. For non-linear adsorption isotherm, the partition coefficient \( K_p \) is used. For linear adsorption isotherm, the distribution coefficient \( K_d \) rather than \( K_p \) is used and Equation 2.5 will be written as:

\[ S = K_d C \]  \hspace{1cm} (2.6)
These coefficients represent the slope of the adsorption isotherm curve and can be determined by differentiating Equation 2.5 with respect to the equilibrium concentration as follows:

\[ K_p \text{ or } K_d = \frac{\partial S}{\partial C} \quad (2.7) \]

Equation 2.7 represents the slope of a line that is tangent to the adsorption isotherm curve at a certain concentration value. As a result, it can be seen that the value of the partition coefficient will change by changing the equilibrium concentration, while the distribution coefficient will maintain a constant value throughout the test. That is why the linear adsorption isotherm relation is always used.

Figure 2.6 Classical typical set of adsorption isotherms
(where q is the amount of sorbed species and C is the equilibrium concentration)
For the non-linear adsorption isotherms several relations have been developed, the most common adsorption isotherm equations are: the Freundlich and the Langmuir equations (Yong et al. 1992).

The Freundlich adsorption isotherm equation is given by the following relation:

\[ S = K_f C^N \] (2.8)

where \( K_f \) and \( N \) are the parameters used to best fit the Freundlich adsorption isotherm equation. The values of \( K_f \) and \( N \) can be determined by plotting the experimental data as \( S \) versus \( C \) on a logarithmic scale, or by using the logarithmic form of Equation 2.8, which is expressed as follow:

\[ \log S = \log K_f + N \log C \] (2.9)

Equation 2.9 shows that \( N \) represents the value of the slope of the best fitted curve, and \( \log K_f \) represents the \( y \)-intercept.

The Langmuir adsorption isotherm equation is given by the following relation:

\[ S = \frac{K_L M C}{1 + K_L C} \] (2.10)
where $K_L$ and $M$ are the parameters used to best fit the Langmuir adsorption isotherm equation. The values of $K_L$ and $M$ can be determined by plotting the experimental data as $C$ versus $C/S$ and fitting the Equation 2.10 by using the following relation:

$$\frac{C}{S} = \frac{1}{K_L M} + \frac{C}{M}$$

(2.11)

The Freundlich adsorption isotherm equation is used more frequently because of its ease of use. When the parameter $N$ is equal to one, the $K_f$ parameter will become equal to the distribution coefficient $K_c$.

2.1.5 Distribution of ions in clay water system

In dry clay, adsorbed cations are clustered on the surface of the clay particles and the excess of those needed to neutralize the surface of the clay particle are present as precipitated salt. When water is added to the clay the cations and a small number of anions will float around the clay particles. The concentration of the adsorbed cations are found to be maximum near the surface and tend to decrease away from the surface of the clay particle. Anions are repelled from the surface of the clay and its concentration is found to be minimum near the surface and have the tendency to increase in concentration away from surface of the particle. This distribution of cations and anions together is termed diffuse double layer; this is illustrated in Figure 2.7. This process (of diffusing ions) effects mainly the viscosity of the diffusing media, as will be discussed in later chapters.
Figure 2.7. Diffuse double layer
( Goldman et al. 1990 )
Several theories have been proposed for the description of ion distributions, but the Gouy-Chapman theory received the greatest attention. The Gouy-Chapman theory assumes the negative charges are distributed uniformly over the surface of the clay particles and the cations and the anions are dispersed in the liquid layer adjacent to the clay particles. In this theory, the attraction between the surface of the clay particles and the adsorbed cations result in a layer of cations at the surface, termed stern layer, and a diffuse layer of cations in solution, termed Gouy layer or double layer. The thickness of the stern layer is fixed and equal to the hydrated radius of the adsorbed cations and the thickness of the double layer can be calculated from (Mitchell 1976):

\[
H = \frac{\zeta kT}{\sqrt{8\pi n_o e^2 Z^2}}
\]  

(2.12)

where \( H \) = thickness of the double layer.

\( \zeta \) = dielectric constant of the media.

\( k \) = Boltzman constant.

\( T \) = temperature in degrees Kelvin.

\( n_o \) = electrolyte concentration in bulk liquid.

\( e \) = unit electric charge.

\( Z \) = charge valance.

Based on the Gouy-Chapman theory, the thickness of the double layer varies by changing some of the variables such as: electrolyte concentration, charge valance, dielectric constant and temperature. The effect of these variables are illustrated in Figure 2.8.
Figure 2.8. Effect of changes in system properties on Diffuse Double Layer
(Mitchell 1970)
2.2 Diffusion In Pure Liquid

In porous media contaminants can diffuse in both solids and liquid. Solid diffusion was neglected from this study (see section 2.1.3) thus liquid diffusion will only be considered. This section will proceed in discussing deeply the diffusion process of contaminants in pure liquid media, i.e. no solid matrix. The discussion begins by introducing the basic relationships for diffusion, then, the more fundamental equations that describes the diffusion in different solutions are presented and discussed.

2.2.1 Basic Relationships For Diffusion

The diffusion of contaminants in a solution is usually assumed to occur due to the difference in concentration. Suppose that $Q$ represents the amount of contaminants that pass through a perpendicular cross sectional area $A$, as shown in Figure 2.9. Then, the rate of change in $Q/A$ per unit time is called flux, $J$, and it is defined as:

$$J = \frac{d\left(\frac{Q}{A}\right)}{dt}$$  \hspace{2cm} (2.13)

The migration of contaminants through an aqueous media or free solution (i.e. no solid matrix) is assumed to take place in accordance with Fick's first law, and it is expressed mathematically in 3-dimensions, as follows (Jost 1960):
\[ J = - D_o \left( \frac{\partial C}{\partial x} + \frac{\partial C}{\partial y} + \frac{\partial C}{\partial z} \right) \]  
\[ J = - D_o \, \text{grad} \, C \]  
\[ J = - D_o \, \nabla C \]  

where \( J \) is the flux, which is the mass of contaminant species passing through a perpendicular cross sectional area per unit time, \( D_o \) is the molecular or the free-solution diffusion coefficient, \( C \) is the concentration of contaminant at this particular distance, and \( \text{grad} \, C \) or \( \nabla C \) is the concentration gradient in the direction of flow, i.e. the change in concentration per unit distance. The negative sign in Equation 2.14 indicates that the diffusion process occurs in the direction of decreasing concentration, as illustrated in Figure 2.10. Fick's first law applies to a steady state transport and the molecular diffusion coefficient is assumed to be constant and isotropic.

If it is assumed that the diffusion coefficient of contaminant species occurs in one direction, say the \( X \) direction, then Fick's first law can be written as follows (Jost 1960):

\[ J = - D_o \, \frac{\partial C}{\partial X} \]  

(2.15)

where \( X \) is the direction of the concentration gradient. Equation 2.15 represents the one dimensional form of Fick's first law of diffusion and it will be used through out the remainder of this study.
Figure 2.9 Cross sectional area

Figure 2.10 Decreasing concentration profile
The flux equation can be described in so many ways. For example, the flux can be described by the mean velocity of the diffusing species $V_m$, where $V_m$ is not the velocity of individual species but it is the sum of the transport rates of all the species that exist in a certain volume divided by the number of species. If the whole liquid is at rest, then the flux equation can be expressed as follows (Erdey-Gruz 1974):

$$J = C \ast V_m$$  \hfill (2.16)

### 2.2.1.1 Diffusion In Ideal Solution

In an ideal solution (i.e. microscopic scale, infinite dilution), the hydrodynamic theory of diffusion considers the liquid to be a continuum, and the diffusion flux is determined by equating the driving force and the frictional resistance force. According to Sutherland and Einstein (1951), the osmotic pressure is regarded as the driving force. As a result, the change of the chemical potential (gradient potential) can be taken here as the driving force. The change in the chemical potential can be determined from the change in concentration gradient as follows (Erdey-Gruz 1974):

$$\Psi_i = \Psi_i^0 + RT \ln a_i$$  \hfill (2.17)

where $\Psi_i^0$ is the standard state chemical potential of the ith species, $R$ is the universal gas constant, and $a_i$ is the activity of the ith species. The activity and the concentration of the ith species are linked together by the following relation (Jost 1960): $a_i = \alpha_i \ast C_i$,
where \( \alpha' \) is the activity coefficient of the ith specie at a given point in the mixture. As the concentration of the ith species becomes more diluted, the activity coefficient approaches unity, i.e. \( \alpha' \to 1 \) and \( a_i \to C_i \). Therefore, the change of the chemical potential in an ideal solution (in one dimension) is:

\[
\partial \Psi_i = RT \partial \ln C_i \tag{2.18}
\]

and the total driving force \( F_d \) per mole of species can be written as (Erdey-Gruz 1974):

\[
F_d = \frac{\partial \Psi}{\partial x} = \frac{RT}{C_i} \frac{\partial C_i}{\partial x} \tag{2.19}
\]

The absolute mobility of the particles is often used instead of the frictional resistance. The absolute mobility of a particular species \( U \) is defined as the limiting velocity \( V \) under a unit force \( f \) (Robinson and Stokes 1959) and it is expressed as follows:

\[
U = \frac{V}{f} \tag{2.20}
\]

rearranging the above equation for \( f \), the unit force will become:

\[
F_r = N \frac{V}{U} \tag{2.21}
\]

where \( F_r \) is the required force per unit mole of species (\( Nf \)) and \( N \) is the avogadro's number. The diffusive flux was previously defined as \( J = V^*C \), thus, by combining this
equation with Equations 2.19 and Equation 2.21 a more fundamental form for the flux equation is produced (Jost 1960):

\[ J = - \frac{URT}{N} \frac{\partial C}{\partial X} \]  \hspace{1cm} (2.22)

By comparing Equation 2.22 with Fick's first law, one can see that the free-solution diffusion coefficient \( D_0 \) is given by:

\[ D_0 = \frac{URT}{N} = U k T \]  \hspace{1cm} (2.23)

where \( k \) is the Boltzmann constant (R/N). Equation 2.23 is known as the Nernst-Einstein equation (Jost 1960); it shows that \( D_0 \) is directly proportional to the absolute temperature of the solution, i.e. the free-solution diffusion coefficient will increase as the temperature of the solution increases as is shown in Table 2.2.

The frictional resistance is found to be extremely difficult to be calculated. This difficulty is mainly attributed to the lack of knowledge of the liquid structure. Therefore, in the calculation of the free-solution diffusion coefficient the assumption applied regarding the frictional resistance is approximate and of limited validity (Erdey-Gruz 1974). One of the approximated methods has been suggested by Stokes (1850), where he calculated the frictional resistance acting on a spherical body moving in a continuum solution. This frictional resistance was found to be dependent on the radius \( r \) of the sphere, the viscosity
\( \mu \) of the solvent, and on the sliding frictional coefficient \( \beta \) between the sphere and the liquid. The frictional resistance was then defined (according to Stokes 1850) as:

\[
f_s = 6 \pi \mu r \left( \frac{1 + \frac{2 \mu}{\beta r}}{1 + \frac{3 \mu}{\beta r}} \right)
\]

(2.24)

If the liquid is entirely wetting the sphere particles moving through it, then \( \beta = \infty \), and the frictional resistance equation becomes:

\[
f_s = 6 \pi \mu r
\]

(2.25)

If the liquid does not completely wet the sphere particles moving through it, then the frictional resistance equation becomes (Erdey-Gruz 1974):

\[
f_s = 4 \pi \mu r
\]

(2.26)

Sutherland suggested that \( \beta = \infty \) for the large spherical symmetrical species in a solvent with small species, under these condition Equation 2.25 holds for the frictional resistance \( f_s \). The mobility of a particle can also be defined in terms of the frictional resistance force due to the viscosity of a solution, as follows: \( U = \frac{1}{f_s} \). Therefore, according to Nernst-Einstein expression, Equation 2.23, the free-solution diffusion coefficient can be written as:
Table 2.2 Free solution diffusion coefficient for some cations and anions at finite dilution in water

<table>
<thead>
<tr>
<th>Cations</th>
<th>( D_0 ) 10^9 cm^2 / sec</th>
<th>Anions</th>
<th>( D_0 ) 10^9 cm^2 / sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>H^+</td>
<td>56.1</td>
<td>OH</td>
<td>25.6</td>
</tr>
<tr>
<td>Li^+</td>
<td>4.72</td>
<td>F</td>
<td>12.1</td>
</tr>
<tr>
<td>Na^+</td>
<td>6.27</td>
<td>Cl^−</td>
<td>10.1</td>
</tr>
<tr>
<td>K^+</td>
<td>9.86</td>
<td>Br^−</td>
<td>10.5</td>
</tr>
<tr>
<td>Rb^+</td>
<td>10.6</td>
<td>I^−</td>
<td>10.3</td>
</tr>
<tr>
<td>Cs^+</td>
<td>10.6</td>
<td>IO_3^−</td>
<td>5.05</td>
</tr>
<tr>
<td>NH_4^+</td>
<td>9.8</td>
<td>Hs^−</td>
<td>9.75</td>
</tr>
<tr>
<td>Ag^+</td>
<td>8.5</td>
<td>S^−</td>
<td>6.95</td>
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<td>Ti^4+</td>
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</tr>
<tr>
<td>Cu(OH)^+</td>
<td>5.3</td>
<td>SO_4^2−</td>
<td>5</td>
</tr>
<tr>
<td>Zn(OH)^2−</td>
<td>8.54</td>
<td>SeO_4^2−</td>
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</tr>
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<td>Be^2+</td>
<td>3.64</td>
<td>NO_2^−</td>
<td>15.3</td>
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<tr>
<td>Mg^2+</td>
<td>3.56</td>
<td>NO_3^−</td>
<td>19.1</td>
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<tr>
<td>Ca^2+</td>
<td>3.73</td>
<td>HCO_3^−</td>
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</tr>
<tr>
<td>Ba^2+</td>
<td>4.04</td>
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<td>Ra^2+</td>
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<td>Mn^2+</td>
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</tr>
<tr>
<td>Fe^{2+}</td>
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<td>H_2SO_4</td>
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<td>Ni^{2+}</td>
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<td>CrO_4^2−</td>
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</tr>
<tr>
<td>Al^{3+}</td>
<td>3.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Th^{4+}</td>
<td>1.53</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^2\) From Lerman 1979
\[ D_o = \frac{KT}{6\pi\mu r} \]  \hspace{1cm} (2.27)

Equation 2.27 is known as Stokes-Einstein equation. Although Stokes-Einstein equation is restricted by several assumptions (such as spherical particles and ideal continuum solvent) it shows that the free-solution diffusion coefficient \( D_o \) is affected by the temperature, viscosity and species size. The smaller the radius of the contaminant species the faster it will transport or diffuse through the aqueous media.

The absolute mobility of particular species is also found to be related to the equivalent ionic conductivity \( \lambda \) by the following relation (Robinson and Stokes 1959):

\[ U = \frac{N\lambda}{|Z| F^2} \]  \hspace{1cm} (2.28)

where \( F \) is the Faraday, \( |Z| \) is the absolute charge valance and \( \lambda \) is the ionic equivalent conductivity. In an ideal solution, at infinite dilution, \( \lambda \) approaches \( \lambda^0 \). If \( \lambda^0 \) is substituted in Equation 2.28 instead of \( \lambda \) and combined with Equations 2.23, the following equation is obtained (Jost 1960):

\[ D_o = \frac{RT\lambda^0}{|Z| F^2} \]  \hspace{1cm} (2.29)
Equation 2.29 is known as Nernst equation. Nernst equation shows that the free solution diffusion coefficient can be calculated if the ionic equivalent conductivity $\lambda^e$ is known. $D_o$ values calculated according to Equation 2.29 are represented in Table A.2.

Effect of viscosity

The frictional resistance can also be related to the viscosity by the following relation (Robinson and Stocks 1959):

$$f_s = \zeta \mu$$

(2.30)

where $\zeta$ is a parameter with a dimension of length which does not depend on the concentration. Therefore the free-solution diffusion coefficient will become:

$$D_o = \frac{RT}{N \zeta \mu} = \frac{K T}{\zeta \mu}$$

(2.31)

Equation 2.31 shows that the free-solution diffusion coefficient is inversely related to the viscosity of the solution, i.e. as the viscosity of the solution increases, the free-solution diffusion coefficient decreases and vica versa.
Effect of Pressure

Changing the pressure can affect the measured value of the free-solution diffusion coefficient. The effect of the pressure can be determined from the changes in the viscosity by using the following relation, while other parameters are fixed (Erdey-Gruz 1974):

\[ \frac{D_{p2}}{D_{p0}} = \frac{\mu_{p0}}{\mu_{p2}} \]  \hspace{1cm} (2.32)

where \( \mu \) is the viscosity. However, the effect of pressure on the measured value of the diffusion coefficient is found to be small. For example, the self-diffusion coefficient of water at 30°C is decreased by a factor of 2% when the pressure is raised from 1 to 1000 atm (Lerman 1979).

2.2.1.2 Diffusion In Non-Ideal Solutions

The equations that have been discussed in the previous sections are valid for ideal and diluted solutions. In ideal solutions, the change in the chemical potential is taken to represent the driving force. This change in the chemical potential has been determined not only by the concentration difference, but also by the activity of the mixture \( a \), and the activity coefficient \( \gamma \). Since the activity coefficient changes when the composition of the mixture changes, the relationship between the activity and the concentration also changes.

For non-ideal solutions, the change in the chemical potential of a solution, i.e. the driving force, can be calculated from the following relation (Erdey-Gruz 1974):
\[(\text{grad } \Psi)_{T,P} = \frac{R T}{C} \left( 1 + \left( \frac{\partial \ln A}{\partial \ln C} \right)_{T,P} \right) \text{grad } C \quad (2.33)\]

where the terms \(T,P\) means at constant temperature and pressure respectively. Thus, the diffusion coefficient can be calculated from the following:

\[D = \frac{K_T}{f_s} B = D_o B \quad (2.34)\]

where \(D_o\) is the free-solution diffusion coefficient calculated from the ideal behavior of the solution and \(B\) is a dummy variable.

When two species are allowed to diffuse, they will diffuse in opposing directions (i.e. the solution diffuses in the opposite direction of the solute). This movement should now be considered since the parameter \(\zeta\) in Equation 2.30 (which describes the frictional resistance) is no longer similar for both components. According to this, the relationship between the diffusion coefficient and the mole fraction of the two components can be expressed as follows:

\[\text{The mole fraction of a component defined as the ratio of the number of moles of a given solute species to the total number of moles of all the components in the solution, and it is expressed as follows: } m_r = m_i / \sum m_i,\]
\[ D_o = \frac{K_T}{\mu} \left( \frac{\partial \ln A_2 m_{r2}}{\partial \ln m_{r2}} \right)_{T,P} \left( \frac{m_{r1}}{\zeta_2} + \frac{m_{r2}}{\zeta_1} \right) \]  \hspace{1cm} (2.35)

where \( A_1 \) and \( A_2 \) are the activity coefficients for the first and second component respectively. If \( \zeta_1 \) and \( \zeta_2 \) are independent of the concentration the above equation becomes:

\[ D_o \mu = \left( \frac{\partial \ln A_2 m_{r2}}{\partial \ln m_{r2}} \right)_{T,P} (m_{r1} \mu_1 D_1 + m_{r2} \mu_2 D_2) \]  \hspace{1cm} (2.36)

Therefore, the \( D_o \) value reported in Table 2.2 represents the maximum value that could be attained under ideal conditions, but this is not the case under non-ideal conditions. Under non-ideal conditions several of the negligible ideal condition factors become important. This is due to (Robinson and Stocks 1959): (1) the effect of electroneutrality and (2) the effect of concentration.

### 2.2.1.2.1 Effect of Electroneutrality

Both diffusion and electrical conductance are involved in the movement of ions in a solution. The main difference between these two processes are:

1) In the conductance process the positive and the negative ions move in opposite directions, whereas in the diffusion process the positive and the negative ions move in the same direction.
2) In the conductance process the ions move independently of one another, while in the diffusion process the ions move at the same speed.

3) In the conductance process the electrical field is the driving force, but in the diffusion process the concentration gradient is the driving force.

It is known that the diffusion coefficient of mobile ions is greater than that for less mobile or immobile ions. This results in increasing the speed of the slower ions and decreasing the speed of the faster ions. Therefore, the diffusion of a single electrolyte, which requires the anions and the cations to diffuse at the same speed or rate, will result in exerting another force due to the gradient in the electrical potential between the motion of the oppositely charged particles (in addition to the force that is due to the chemical gradient). Therefore, the free-solution diffusion coefficient $D_o$ should be modified to account for this additional force. This modification has been done by Robinson and Stokes (1959) by the following equation:

$$D_{o12} = \frac{RT}{F^2} \frac{(|Z_1| + |Z_2|)}{|Z_1Z_2|} \frac{\lambda_1\lambda_2}{\lambda_1 + \lambda_2}$$  \hspace{1cm} (2.37)

where $D_{o12}$ is the free-solution diffusion coefficient for a single electrolyte diffusing in one direction in a finite dilution. The free-solution diffusion coefficient for two different ions with the same valance and the same concentration gradient, diffusing against each other can be calculated as follows (Jost 1960):
\[ D_{012} = \frac{(C_1 + C_2)D_{o1}D_{o2}}{D_{o1}C_1 + D_{o2}C_2} \]  \hspace{1cm} (2.38)

where \( D_{o1} \) and \( D_{o2} \) are the free-solution diffusion coefficients of the respective ions in a finite dilution. But, if the two ions have different valences then the free-solution diffusion coefficient is calculated from (Robinson and Stock 1959):

\[ D_{012} = \frac{(|Z_1|C_1 + |Z_2|C_2)D_{o1}D_{o2}}{|Z_1|D_{o1}C_1 + |Z_2|D_{o2}C_2} \]  \hspace{1cm} (2.39)

where \( C_1 \) and \( C_2 \) are the concentrations of the respective ions as equivalent per liter of solution, and \( Z_1 \) and \( Z_2 \) are the valences of the respective ions. The above free-solution diffusion coefficient, \( D_{012} \), is often termed as the inter diffusion or the counter diffusion coefficient.

If more than two ions are present, a general equation can be developed. But this is a difficult process due to the fact that ions will diffuse in an infinite number of ways to satisfy the electroneutrality condition. The effect of the electroneutrality condition on the individual mobility or diffusivity of the ions is shown by comparing the limiting free-solution diffusion coefficient values obtained from Table 2.3 with the free-solution diffusion coefficient values obtained from Table 2.2.
Table 2.3 Free-solution diffusion coefficient of selected aqueous electrolyte solutions at 25°C\(^4\)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>(D_{o12} \times 10^{-10} \text{ cm}^2/\text{sec})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>33.36</td>
</tr>
<tr>
<td>HBr</td>
<td>34</td>
</tr>
<tr>
<td>LiCl</td>
<td>13.66</td>
</tr>
<tr>
<td>LiBr</td>
<td>13.77</td>
</tr>
<tr>
<td>NaCl</td>
<td>16.1</td>
</tr>
<tr>
<td>NaBr</td>
<td>16.25</td>
</tr>
<tr>
<td>NaI</td>
<td>16.14</td>
</tr>
<tr>
<td>KCl</td>
<td>19.93</td>
</tr>
<tr>
<td>KBr</td>
<td>20.16</td>
</tr>
<tr>
<td>KI</td>
<td>19.99</td>
</tr>
<tr>
<td>CsCl</td>
<td>20.44</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>13.35</td>
</tr>
<tr>
<td>BaCl(_2)</td>
<td>13.85</td>
</tr>
<tr>
<td>LaCl(_3)</td>
<td>12.93</td>
</tr>
</tbody>
</table>

\(^4\) From Robinson and Stokes 1959.
2.2.1.2.2 Effect of Concentration

As the concentration of the solution increases, a number of effects negligible for the diluted solutions become more important. These effects are (Erdey-Gruz 1974):

(1) The diffusion of the solvent in the opposite direction of the solutes can no longer be neglected, since the concentration of the solvent is changing too.

(2) Some of the ions may carry with them a permanently attached layer of solvent molecules, which acts as a part of the diffusion solute entity.

(3) The viscous forces may be considerably modified by the presence of a large number of ions.

In case of diluted solutions, the solvents are assumed to be approximately stationary, but this is not the case for concentrated solutions. As the concentration of the solution increases more solute-solute reactions will occur, these reactions were previously described by the activity coefficient $\infty$\>, $\left( a = \infty C \right)$. In concentrated solutions, the activity coefficient is no longer equal to unity, thus the concentration is no longer equal to the activity value. Therefore, the potential gradient in Equation 2.18 and Equation 2.19 should be modified to account for $\infty C$ instead of $C$. As a result, the diffusion coefficient of electrolytes should also be modified. The diffusion coefficient of concentrated electrolytes has been modified as follows (Robinson and Stokes 1959):

$$D_{12} = \frac{RT}{F^2} \left( \frac{[Z_1] + [Z_2]}{|Z_1||Z_2|} \right) \frac{\lambda_1\lambda_2}{\lambda_1 + \lambda_2} \left( 1 + \frac{\partial \ln \lambda_{m12}}{\partial \ln C_{12}} \right)$$

(2.40)
Equation 2.40 is called Nernst-Hartley equation and can be reduced to a much simpler form as follows:

\[ D_{12} = D_{\text{sol}} \left( 1 + \frac{\partial \ln \lambda_{m12}}{\partial \ln C_{12}} \right) \quad (2.41) \]

where \( D_{12} \) is the diffusion coefficient of the concentrated electrolyte, \( D_{\text{sol}} \) is the free-solution diffusion coefficient of a single electrolyte (see Equation 2.37), \( C_{12} \) is the concentration of the single electrolyte and \( \lambda_{m12} \) is the mean ionic conductivity coefficient on molarity scale. Figure 2.11 shows the effect of solution concentration on the value of the diffusion coefficient in non-ideal solutions.

![Graph showing concentration dependence of diffusion coefficient](image)

**Figure 2.11** Concentration dependence of diffusion coefficient in diluted solution at 25°C for sum electrolytes (where \( D \) is the diffusion coefficient and \( C \) is the concentration of electrolytes)
2.2.2 Fick's Second Law

Fick's first law can not be used to measure the contaminant diffusion coefficient with respect to time. Fick's first law is sufficient to describe only the steady-state diffusion, i.e. \( \frac{\partial C}{\partial t} = 0 \). For transient-state diffusion, i.e. \( \frac{\partial C}{\partial t} \neq 0 \), Fick's first law need to be modified.

If the species concentration changes with a zone of constant cross-sectional area, \( A \), which has a length of \( \Delta X \) (as shown in Figure 2.12), then any changes in the amount of species in this zone will equal to:

\[
\Delta Q = Q_{\text{in}} - Q_{\text{out}} = (J_{\text{in}} - J_{\text{out}})A \Delta t
\]

(2.42)

\( \Delta Q \) is also equal to the product of the volume of the zone and the change in concentration in the zone, i.e. \( \Delta Q = A \Delta X \Delta C \). By equating this equation and Equation 2.42 and substituting Fick's first law, the following relation is obtained:

\[
D_0 = \left[ \left( \frac{\partial C}{\partial X} \right)_{X=0} - \left( \frac{\partial C}{\partial X} \right)_{X=\Delta X} \right] \frac{\Delta C}{\Delta X} \frac{\Delta X}{\Delta t} = \frac{\Delta C}{\Delta t}
\]

(2.43)

By integrating the above equation with respect to distance and time and taking the limit of \( \Delta X \) and \( \Delta t \) approaches to zero, Equation 2.43 reduces to:
\[
\frac{\partial c}{\partial t} = \text{div} \left( D_o \text{ grad } c \right)
\]  

(2.44)

where \( t \) is the time. The above equation is known as Fick's second law and it applies to the transient-state diffusion coefficient of ionic species at infinite dilution in three dimensions.

For one dimensional diffusion coefficient (say \( X \)-direction) Equation 2.44 reduces to:

\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D_o \frac{\partial c}{\partial x} \right)
\]  

(2.45)

For constant cross-sectional area \( A \), and assuming that \( D_o \) is independent on the concentration of the species, Equation 2.45 becomes:

\[
\frac{\partial c}{\partial t} = D_o \frac{\partial^2 c}{\partial x^2}
\]  

(2.46)

Figure 2.12 Cross-sectional area of a unit volume
The above equation is a differential equation whose solution describes the concentration of a system as a function of time and distance. The solution of this equation depends on the boundary condition and the free-solution diffusion coefficient.

2.2.3 Types of Diffusion

There are mainly four different types of free-solution diffusion coefficient which may be measured, they are (Shackelford et al. 1991):

1) Self-diffusion.
2) Tracer-diffusion.
3) Salt-diffusion.
4) Counter-diffusion or interdiffusion.

Figure 2.13 schematically illustrates the four different types of systems that is used to describe the four different types of diffusion coefficients. The type of diffusion coefficient which is to be measured depends on the system used to measure it. A brief description of each type of the diffusion system follows.

2.2.3.1 Self-Diffusion

Figure 2.13 (a) shows a schematic illustration of the self-diffusion system. A true self-diffusion system is initially composed of two half cells containing equal concentrations of sodium chloride. The movement of the species in this system would be truly random, but this motion can not be traced. Therefore, an isotope has been introduced in one of the
Before Diffusion | After Diffusion
---|---
$^{22}\text{NaCl}$ $\text{NaCl}$ $^{22}\text{Na}^+$ $\text{Na}^+$
$\text{NaCl}$ $^{42}\text{KCl}$ $\text{NaCl}$ $^{42}\text{K}^+$ $\text{Na}^+$
$\text{NaCl}$ $\text{Water}$ $\text{Na}^+$ $\text{Cl}^-$
$\text{NaCl}$ $\text{KCl}$ $\text{Na}^+$ $\text{K}^+$

**Self-Diffusion**

**Tracer-Diffusion**

**Salt-Diffusion**

**Counter-diffusion or Interdiffusion**

Figure 2.13 Schematic illustration of the four different types of the diffusion coefficients
half cells in order to simulate the movement of the isotope species in the self-diffusion system. This simulation is done by replacing a small amount of the sodium Na\(^+\) in one of the half cells by an equal amount of its isotope \(^{22}\text{Na}^+\). After connecting the two half cells, diffusion of both Na\(^+\) and its isotope \(^{22}\text{Na}^+\) will occur. Their movements are in opposite direction of each other. This type of diffusion occurs due to the small concentration gradients that exists for each type of the species (Na\(^+\) and \(^{22}\text{Na}^+\)). Since the concentration gradient is very small, the movement of the tracer \(^{22}\text{Na}^+\) and the solute Na\(^+\) is not effected by the movement of the ions of the opposite charge Cl\(^-\). The tracer in this system can be considered to be diffusing in a stationary background of non-diffusing ions. This movement of ions is termed as self-diffusion and the diffusion described in this system referred to as the self-diffusion coefficient.

### 2.2.3.2 Tracer-Diffusion

The tracer-diffusion system is similar to the self-diffusion system, except the isotope species here are composed of different species. Figure 2.13 (b) illustrates schematically the tracer-diffusion system. In this system a small amount of the Na\(^+\) in one of the half cells has been replaced by an equal amount of a different isotope, such as \(^{42}\text{K}^+\). After connecting the two half cells, the isotope \(^{42}\text{K}^+\) will move from the region of higher concentration to the region of lower concentration (left to right), while the solution Na\(^+\) will move in the opposite direction. This type of diffusion occurs due to the difference in the concentration gradient for each type of species (Na\(^+\) and \(^{42}\text{K}^+\)). The movements of these ions in this system are referred to as the tracer-diffusion and the diffusion coefficient.
described in this system is termed tracer-diffusion coefficient. At an infinite dilution the value obtained from the tracer-diffusion and the self-diffusion is equal.

2.2.3.3 Salt-Diffusion

A schematic illustration for the salt-diffusion system is shown in figure 2.13 (c). In this system one of the half cells contains sodium chloride while the other half contains the solvent only. After connecting the two half cells, both Na⁺ and Cl⁻ will diffuse in the same direction until an equilibrium condition is reached. In this type of diffusing system the electroneutrality condition becomes important. The movement in this system is referred to as salt-diffusion and the diffusion coefficient described in this system is termed salt-diffusion coefficient.

2.2.3.4 Counter-diffusion or Interdiffusion

Counter-diffusion or interdiffusion describes the process where by different ions of the same charge are diffusing against each other, or diffusing in the opposite direction of each other. Figure 2.13 (d) shows a schematic illustration for the counter-diffusion system. This system is composed of two half cells containing the same concentration of sodium chloride NaCl and potassium chloride KCl. After connecting the two half cells together, the sodium Na⁺ will diffuse in the opposite direction of the potassium K⁺. This diffusion process occurs due to the difference in their concentration gradients. The movement of species in this system is referred to as counter-diffusion or interdiffusion and the diffusion
coefficient described in this system is termed counter-diffusion or interdiffusion coefficient.

In landfill disposal sites, the practical field problems are best represented by both salt-diffusion and tracer-diffusion; whereas, tracer-diffusion best represents most of the practical field problems in nuclear waste disposal vault because the groundwater's chemical composition is likely to be the same and the concentration of contaminants is low.
2.3 Diffusion In Porous Media

Fick's (1855) theory showed that the diffusional transport of substances through solutions obeys the same mathematical law that Fourier had derived for the conduction of heat in solids. Since that time, several theoretical and experimental aspects of diffusion have been undergone for both single and multi-phase systems. Single systems are mainly composed of liquids, while multi-phase systems are composed of liquid and soil particles. In multi-phase systems the diffusion process usually takes place through the liquid media.

Diffusion of contaminant species in a soil matrix is found to be slower than that in pure liquid. This difference can be attributed to the following reasons:

1. reduction in the cross-sectional area of diffusing flow.

2. diffusion pathway is more tortuous due to the presence of the solid matrix and the nature of the porous media.

3. there may be a reduction in the mobility of the species in the soil matrix due to the interaction between the diffusing species and the soil matrix.

Figure 2.14 illustrates the effect of the porous media on the diffusion process and it gives a brief explanation for the first two reasons. The third reason is usually associated with the adsorption-desorption reactions between the diffusing species and the clay particles (soil particle), as was discussed in section 2.1.4.1.
Figure 2.14 Effect of porous media on the Diffusion process:
(a) Diffusion in homogeneous solution
(b) Diffusion in porous media
Due to the reasons pointed out, Fick's first and second law of diffusion in free solution can not be used in porous media. These laws should be modified to describe the diffusion of contaminant species in soil or porous media. The modifications of Fick's laws that allow the description of diffusion in porous media are discussed in the following sections.

2.3.1 Modifying Fick's First law

Fick's first law of diffusion should be modified in several ways to account for the diffusion process in porous media. These modifications are discussed below.

2.3.1.1 Reduction in The Cross-Sectional Area of Flow

In the steady-state condition, when the concentration distribution is assumed to be linear with distance, the diffusive flux is expressed as follows:

\[ J = -D_o \frac{\partial C}{\partial x} \]  \hspace{1cm} (2.47)

where \( D_o \) is the free-solution diffusion coefficient and \( C \) is the concentration of the diffusing species in the aqueous phase of the pore space. The flux was previously defined as the rate of transport of species per unit cross-sectional area of flow. Therefore, the flux should also be modified to account for this reduction in the cross-sectional area. The modification can be done as follows (Jost 1960):
\[ J = -D_0 \eta \frac{\partial C}{\partial X} \]  \hspace{1cm} (2.48)

where \( \eta \) is the volumetric water content. The volumetric water content is defined as the volume of water per unit volume of soil and is expressed as: \( \eta = \theta S_r \), where \( \theta \) is the total porosity (which is defined as the total volume of voids over the total volume of soil specimen) and \( S_r \) is the degree of saturation. By substituting this into Equation 2.48, the following equation results:

\[ J = -D_0 \theta S_r \frac{\partial C}{\partial X} \]  \hspace{1cm} (2.49)

The above equation shows that the diffusive flux will be at its maximum when the degree of saturation \( S_r \) is equal to unity (saturated soil) while the remaining parameters are fixed.

2.3.1.2 Effect of Diffusion Pathway

The tortuosity factor has two effects on the diffusion process, they are:

1) Effect on the cross-sectional area that is perpendicular to direction of the diffusion flow.

2) Effect on the driving force (concentration gradient) due to the long diffusion pathway rather than the actual pathway.
Each of these effects are illustrated in Figure 2.15 and Figure 2.16. In order to describe the diffusion process in porous media Equation 2.49 should also be modified to account for these effects. The modification can be proceeded as follows:

\[ J = -D_o \theta_s S_r \frac{\partial C}{\partial X_e} \]  \hspace{1cm} (2.50)

where \( \theta_e \) is the effective porosity (actual or real porosity not the total) and \( X_e \) is the effective diffusion pathway (actual diffusion pathway). From Figure 2.16 \( \theta_e = \frac{L}{L_e} \theta \) and \( X_e = \frac{L}{L_e} X \), thus Equation 2.50 can be written as follows:

\[ J = -D_o \frac{L}{L_e} \left( \frac{L}{L_e} \right)^2 \theta_s S_r \frac{\partial C}{\partial X} \]  \hspace{1cm} (2.51)

In Equation 2.51 the factor \( \left( \frac{L}{L_e} \right)^2 \) is termed the tortuosity factor and is represented by the symbol \( \tau \). The tortuosity factor \( \tau \) has been defined in so many different ways. No matter how the tortuosity factor is defined, care should be taken to ensure that the proper tortuosity factor has been chosen for the correct diffusion expression. The tortuosity factor \( \tau \) in this study is chosen to be equal to: \( \tau = \left( \frac{L}{L_e} \right)^2 \). Thus Equation 2.51 can be expressed as:

\[ J = -D_o \tau \theta_s S_r \frac{\partial C}{\partial X} \]  \hspace{1cm} (2.52)
Figure 2.15  Effective Length in Porous Media
Porosity Effect:
\[ \theta = \frac{a_1}{A} \]
\[ a_2 = \frac{L}{Le} \cdot a_1 \]
\[ \theta_e = \frac{a_2}{A} \]
\[ \theta_e = \frac{L}{Le} \cdot \theta \]

Concentration Gradient Effect:
\[ \Delta X = L = X_2 - X_1 \]
\[ \Delta X_e = Le \]
\[ \Delta X_e / Le = \Delta X / L \]
\[ \Delta X_e = (Le / L) \cdot \Delta X \]
\[ \Delta C / \Delta X_e = \Delta C [Le / L \cdot \Delta X] \]
\[ \Delta C / \Delta X_e = (L / Le) \cdot \Delta C / \Delta X \]

A, a1, a2 = areas
L, Le, \( \Delta X \), \( \Delta X_e \) = lengths
C = concentration
\( \theta \) = total porosity \( \theta_e \) = effective porosity

Figure 2.16 Effect of tortuous pathway on diffusion process
2.3.2 Pore Diffusion Coefficient

At present, the tortuosity factor can not be measured independently. Therefore, some researchers preferred to group the tortuosity factor with other factors in a single term. This term is defined as the pore diffusion coefficient and it is represented by $D_p$. In this study, the pore diffusion coefficient is defined as:

$$D_p = D_0 \tau$$  \hspace{1cm} (2.53)

By substituting Equation 2.53 into Equation 2.52, the diffusive flux equation becomes:

$$J = -D_p \theta S_r \frac{\partial C}{\partial X}$$  \hspace{1cm} (2.54)

There are several other definitions for the pore diffusion coefficient $D_p$, some of these definitions are reported in Table 2.4. No matter which of the pore diffusion coefficient is selected, care should be taken to ensure that the appropriate definition has been chosen. In this study the degree of saturation is assumed to be equal to unity; therefore, the diffusive flux is equal to:

$$J = -D_p \theta^2 \frac{\partial C}{\partial X}$$  \hspace{1cm} (2.55)
Table 2.4 Definitions of the pore diffusion coefficient $D_p$
(Shackelford 1988)

<table>
<thead>
<tr>
<th>Definition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_p = D_o \tau$</td>
<td>Gillham et al. 1984</td>
</tr>
<tr>
<td>$D_p = D_o \alpha/(1/\tau)$</td>
<td>Li and Gregory 1974</td>
</tr>
<tr>
<td>$D_p = D_o \theta/(1/\tau)$</td>
<td>Berner 1971, and Drever 1982</td>
</tr>
<tr>
<td>$D_p = D_o \tau \alpha \gamma \theta$</td>
<td>Kemper et al. 1964, Olsen and Kemper 1968, and Nye 1979</td>
</tr>
<tr>
<td>$D_p = D_o \tau \gamma$</td>
<td>Porter et al. 1960</td>
</tr>
<tr>
<td>$D_p = D_o \tau \alpha \theta$</td>
<td>Van Schaik and Kernper 1966</td>
</tr>
</tbody>
</table>

$D_p$ = pore diffusion coefficient
$D_o$ = free-solution diffusion coefficient
$\tau$ = tortuosity factor ($L / L_e$)$^2$
$L$ = straight line length
$L_e$ = effective length
$\alpha$ = fluidity factor
$\gamma$ = negative adsorption or anion exclusion factor
$\theta$ = volumetric water content
2.3.3 Modifying Fick's Second Law

Fick's first law of diffusion can not be used to measure the diffusion coefficient of contaminant species with respect to time and distance. Therefore, Fick's second law of diffusion, which is the differential equation of Fick's first law with respect to distance, can be used to describe the transient or the time dependent diffusion process. The general relation that describes the rate of change of mass of species for an elemental volume described as follows (Freeze and Cherry 1979):

\[
\text{net rate of change of mass of solute mass} = \text{out of the reaction} \pm \text{due to the reaction} \quad (2.56)
\]

The above equation shows that the transport mechanism of the diffusing species in a porous medium depends on whether the species are conservative (non-reactive, i.e. the diffusing species does not undergoes chemical or biochemical or radioactive reaction) or non-conservative (reactive, i.e. the diffusing species reacts chemically, biochemically or decays radioactively). The chemical and the biochemical reactions that alter the contaminant species concentration during the diffusion process are grouped together into nine categories and are illustrated previously in Figure 2.1.
2.3.3.1 Diffusion of Conservative Species

Since the conservative species are not reactive, the time dependent diffusion equation can be determined by applying the mass balance equation and neglecting any other reactions. This is done as follows ( Freeze and Cherry 1979 ):

\[
\begin{bmatrix}
\text{net change in} \\
\text{the concentration} \\
\text{of the diffused species} \\
\text{per unit time}
\end{bmatrix} = 
\begin{bmatrix}
(\text{flux})_{\text{in}} \\
(\text{flux})_{\text{out}}
\end{bmatrix}
\]  

(2.57)

If it is assumed that the concentration of the contaminant species changes within a zone of constant cross-sectional area \( A \) which has a length of \( \Delta X \) ( as shown in Figure 2.12 ), then any change in the amount of the contaminant species in this zone will be equal to:

\[
\Delta Q = Q_{\text{in}} - Q_{\text{out}} = (J)_{\text{in}} - (J)_{\text{out}} A \Delta t
\]  

(2.58)

\( \Delta Q \) is also equal to the product of the volume of the zone element and the change in the concentration of contaminant that occurs in this zone; it is expressed as follows:

\[
\Delta Q = A \Delta X \Delta C
\]  

(2.59)
By equating Equation 2.58 and Equation 2.59, and by using Equation 2.55 as a base, the following relation can be written:

$$\frac{\Delta C}{\Delta t} = D_p \theta \frac{\left( \frac{\partial C}{\partial x} \right)_{x=0} - \left( \frac{\partial C}{\partial x} \right)_{x=\Delta X}}{\Delta X}$$

(2.60)

By integrating the above equation with respect to distance and time, taking the limit of $\Delta X$ and $\Delta t$ approaches to zero, and assuming that $D_p$ and $\theta$ are constant, the time dependent diffusion equation can be written as:

$$\frac{\partial C}{\partial t} = D_p \theta \frac{\partial^2 C}{\partial x^2}$$

(2.61)

### 2.3.3.2 Diffusion of Non-Conservative Species

For non-conservative species, different types of chemical and/or biochemical reactions may occur during the transport of contaminants in the soil (as described previously). The time dependent diffusion equation for non-conservative species can be determined by modifying Equation 2.61 to account for these reactions. The modifications are as follows (Robinson and Stocks 1959):

$$\frac{\partial C}{\partial t} = D_p \theta \frac{\partial^2 C}{\partial x^2} \pm \Sigma R_c \pm R_t C_i$$

(2.62)
where \( R_r \) is a rate constant used to describe the reaction (radioactive or biological decay) and \( R_s \) is a general term used to describe other chemical or biological reactions. The positive (\( + \)) sign denotes a gain in the concentration (e.g. chemical dissolution) and the negative (\( - \)) sign denotes a loss in the concentration (e.g. radioactive decay, adsorption, precipitation).

The non-conservative species, which diffuse through the soil specimen, have the ability to interact with the surface of the individual soil particle by two mechanisms: (1) ion exchange and (2) adsorption process (see section 2.1.4). Adsorption and radioactive decay are the only types of reactions that can be modeled. Thus, the time dependent diffusion equation can be modified to:

\[
\frac{\partial C}{\partial t} = D_A \frac{\partial^2 C}{\partial X^2} \tag{2.63}
\]

where \( D_A \) is the apparent diffusion coefficient and is equal to \( \frac{D_p}{R} \). Chapter 4 contains a detailed discussion of how this equation was achieved.

### 2.3.4 Summary

The steady-state diffusion in both free solution and porous media are described by Fick's first law. This law was supported by a number of fundamental expressions, such as the Nernst-Einstein, the Nernst and the Einstein-Stokes expressions. The transient-state
diffusion in both free solution and porous media are described by Fick's second law, which is the derivation of Fick's first law to time.

There are mainly four different types of free-solution diffusion coefficients depending on the system being used to measure them. They are: (1) self-diffusion coefficient, (2) tracer-diffusion coefficient, (3) salt-diffusion coefficient and (4) counter-diffusion coefficient. The migration of contaminants from the disposal sites to the surrounding environment is shown to be best represented by tracer-diffusion.
CHAPTER 3

Methodologies To Determine The

Diffusion Coefficient

The fundamental equations used to define the diffusion coefficients have been discussed in previous sections. Before considering the theoretical interpretation of diffusion data, the various experimental methods available for measuring these coefficients will be discussed. These methods can be grouped in several ways, perhaps the most common division is: steady-state methods, which are based on Fick's first law of diffusion, and transient-state methods, which are based on Fick's second law of diffusion.

Fick's first and second laws are known to be applied to homogenous, isotropic and isothermal media. In clay-water system, the diffusion process depends not only on the molecular diffusion in the liquid phase and on the physiochemical processes, such as sorption, precipitation and ionic exchange, but it also depends on the pore size that restrict diffusion, the diffusion pathway and the tortuosity (Cheung et al. 1989). Therefore, the measured values of the contaminant diffusion coefficients are not the same as those of the free-solution diffusion coefficients. These measured values are referred to as the apparent
diffusion coefficients. There are mainly two values for the apparent diffusion coefficient, one for the steady-state $D'_A$ and the other for the transient-state $D_A$.

There are basically three different tracer methods, one for the steady-state and two for the transient-state. These methods are the most commonly used in the laboratory to measure the apparent diffusion coefficients in compacted bentonite; they are described in the following sections.

3.1 Transient-State Diffusion Coefficient

3.1.1 Through-Diffusion Method

In the through-diffusion method a stainless steel cell is used. Figure 3.1 illustrate a diagram of the diffusion cell. The cell is designed to accommodate the swelling pressure which may be generated by wetting the clay sample. The diffusion experiment is conducted by compacting air-dried clay sample in the stainless steel ring to the required density; the steel ring usually has a diameter of 4.12 cm and a height of 1.28 cm (Oscarson et al. 1992). The cell is then assembled and allowed to saturate with a certain solution for a period of at least 3 to 6 weeks. This period is found to be sufficient for saturating the clay soil (Cheung et al. 1989). After this time, one end of the clay sample is brought in contact with a solution that is spiked with a tracer (source reservoir) and the other end is brought in contact with an unspiked solution (collection reservoir). The tracer concentration in the collection reservoir is maintained at zero, while the tracer concentration in the source reservoir is maintained at a constant concentration. When the
Figure 3.1 Diagram of the diffusion cell used in the through-diffusion experiments (Cheung et al. 1988)
activity of the tracer at the collection reservoir becomes constant the cell is disassembled and sectioned into thin slices, 1 to 2 mm in thickness (Oscarson et al. 1992). The tracer concentration and the moisture content in each section are then determined. By assuming that contaminant migration is in x-direction only, the constant diffusive flux can be determined by using Fick's first law of diffusion, i.e. \[ J = -D \frac{\partial C}{\partial x}. \]

Two diffusion coefficients can be calculated from this method depending on the technique used to measure the concentration gradient. If the tracer concentration is measured in each slice, then the apparent diffusion coefficient at the transient-state condition is determined, it is represented by \( D_A \) and is defined as:

\[ D_A = \frac{\Delta X}{\Delta C} \frac{\Delta Q}{\Delta t} \]  

(3.1)

where \( \Delta X / \Delta C \) is the inverse of the concentration gradient. \( D_A \) can also be related to the free-solution diffusion coefficient and the tortuosity factor as (Oscarson et al. 1992):

\[ D_A = \frac{D_0 \tau}{R} \]  

(3.2)

For the initial and boundary conditions, the tracer concentration profile given by Fick's second law can be determined by using the following relation (Crank 1975, Cheung et al. 1988):

\[ \frac{C_i}{C_0} = \text{erfc} \left( \frac{X}{2 \sqrt{D_A t}} \right) \]  

(3.3)
provided that the tracer does not completely penetrate through the clay specimen. There are number of problems associated with this method, especially when bentonite is used. These problems are (Cheung et al. 1989, and Oscarson et al. 1992):

1) It is difficult to maintain a constant concentration for cationic diffusion at the source reservoir due to the high cation exchange capacity, especially at the early stage of the diffusion experiment.

2) The tracer concentration in the end slice of the clay sample may be altered due to the uptake of solution by the clay from the porous plates during disassembling of the diffusion cell.

3) The diffusion process may be effected by the diffusion of solutes (not tracers) from the soil to the external solution.

3.1.2 In-Diffusion Method

In this method the tracer-free soil is brought in contact with either a planar tracer source or an impulse tracer source. This is shown in Figure 3.2 and Figure 3.3.

3.1.2.1 Planar Source

The saturated tracer-free soil is prepared in a similar way to that of the through-diffusion method. The planar source is prepared by making a clay slurry first and placing several drops of this slurry on a glass plate and allowing it to dry. Drops of the solution containing the tracer is then placed on the dried clay slurry and allowed to evaporate until dryness. This stage results in a dry layer of clay containing the tracer.
Finally, the dried clay layer is removed from the glass plate and is placed in the middle of the diffusion cell, separating the two identical tracer-free clay specimen. This is illustrated in Figure 3.2. At this stage, the entire diffusion cell is submerged in the tracer-free solution for diffusion. The cell is left for a predetermined period of time to allow diffusion to take place. After the predetermined period of time elapsed, the diffusion cell is then disassembled and the clay specimen is sectioned into thin slices, 1 to 2 mm in thick and the tracer concentration and the moisture content are determined for each slice (Cheung et al. 1992).

For the initial and boundary conditions\(^5\), the tracer concentration profile given by Fick's second law can be determined by using the following relation (Crank 1975, Torstensenfelt 1986, Cheung et al. 1989):

\[
\frac{C_i}{M} = \frac{0.5}{\sqrt{\pi D_A t}} e^{-\frac{x^2}{4D_A t}}
\]  

(3.4)

provided that the tracer does not completely penetrate the clay specimen. M is the total amount of tracer added to the dried clay layer per unit area.

\(^5\) The initial and boundary conditions are:

\[
C(X,0) = C_0 \quad X = X_o
\]

\[
C(X,0) = 0 \quad X = 0 \text{ and } X = L
\]

\[
\frac{\partial C}{\partial X} = 0 \quad X = 0 \text{ and } X = L
\]

where \(X_o\) is the distance or the point at the mid section (tracer clay layer)
This method can also be used to study the effect of additives on the diffusion process under the same experimental conditions by introducing the additives in one of the tracer-free clay specimen (Cheung et al. 1989).

The possible solute (not tracer) transport across the source-soil interface that occurs in the through-diffusion method is eliminated in this method.

![Diagram of the in diffusion method](image)

Figure 3.2 Diagram of the in diffusion method
Planar Source
3.1.2.2 Impulse Source

In this method, a stainless steel or Plexiglas diffusion cell can be used as illustrated in Figure 3.3. The diffusion experiment is conducted by saturating two half cells, one of the half cells saturated with a tracer-free solution, while the other saturated with the solution plus a tracer. Both half cells are then compacted to the same density. The compacted clay specimen are then allowed to equilibrate in a watertight cell for a period of at least one week (Robin et al. 1987). After the equilibration period, the two cells are brought in contact with each other and left for a predetermined period of time to allow the diffusion to take place. When the predetermined period of time has elapsed, the diffusion cell is then disassembled and the clay specimen is sectioned into thin slices 1 to 2 mm thick. The tracer concentration and the moisture content in each slice are then determined.

For the initial and boundary conditions\(^6\), provided that the tracer does not completely penetrate the clay specimen, the tracer concentration profile given by Fick's second law can be determined by using the following relation (Crank 1975, Gillham et al. 1984):

\[^6\] The initial and boundary conditions are
\[
\begin{align*}
C(X,0) &= C_0, & X < 0 \\
C(X,0) &= 0, & X > 0 \\
C(-\infty,t) &= C_0 \\
C(+\infty,t) &= 0
\end{align*}
\]
\[
\frac{C_i}{C_o} = \frac{1}{2} \text{erfc} \left( \frac{X}{\sqrt{D \Lambda t}} \right)
\] (3.5)

where \(X\) is the distance starting from the interface point. If the tracer does penetrate the clay specimen, then the tracer concentration profile given by Fick's second law can be determined by using the following relation (Crank 1975, Gillham et al. 1984) \(^7\):

\[
\frac{C_i}{C_o} = \frac{X_o}{L} + \frac{2}{\pi} \sum_{\theta}^{\infty} \frac{\exp \left( - \frac{D \Lambda \theta^2 \pi^2 t}{L^2} \right)}{\theta} \cos \left( \frac{\theta \pi X}{L} \right) \sin \left( \frac{\theta \pi X_o}{L} \right)
\] (3.6)

where \(X_o\) is the location of the interface section of the clay specimen in the diffusion cell overall length \(L\).

In this method, diffusion takes place only within the soil, i.e. no solution-soil interface transport is involved. It is noted that the diffusion process may be complicated by water movement in the unsaturated soil specimen due to clay water potential gradient. This effect is small in nearly saturated soil specimen with low hydraulic conductivity. However, the diffusion cell should be perfectly sealed to prevent water from evaporating during the experiment (Cheung et al. 1989).

\(^7\) The initial and boundary conditions are
\[C(X,0) = C_o \quad 0 < X < X_o\]
\[C = 0 \quad X_o < X < L\]
\[\partial C / \partial X = 0 \quad X_n = 0 \text{ and } X = L\]
Figure 3.3 Diagram of the in-diffusion method
Impulse Source
By using this preparation technique, the soil will be less saturated and less homogeneous than the through-diffusion method (Oscarson et al. 1992, Cheung et al. 1992, Cheung et al. 1989).

3.2 Steady-State Diffusion Coefficient

3.2.1 Through-Diffusion Method

In this method, the preparation of the tracer-free clay specimen and the experiment is proceeded in a similar manner as the through-diffusion method in transient-state. In this method, the concentration gradient is measured between the source and the collection reservoirs; the apparent diffusion coefficient $D'_A$ at steady state condition is then determined (discussed in more detail in the following section) and it is expressed as:

$$D'_A = \frac{L}{\Delta C} \frac{\Delta Q}{A \Delta t} \quad (3.7)$$

where $L$ is the length of the clay sample, $A$ is the cross-sectional area of the sample, $\Delta C$ is the difference in the tracer concentration between the source and the collection reservoir, and $\Delta Q$ is the change in the amount of the diffusing species that passes through the clay sample during a period of time $D'_A$ can also be written in terms of the free-solution diffusion coefficient and the tortuosity factor (Oscarson et al. 1992):

$$D'_A = D_0 \tau \theta \quad (3.8)$$
If the change in the tracer concentration in the tracer-free solution or in the collection reservoir is measured, the cumulative amount of the tracer species, $Q$, that passes through the clay specimen can be estimated. For the initial and boundary conditions, the tracer concentration profile given by Fick’s first law can be determined by using the following relation (Eriksen and Jacobsson 1982):

$$C_o = C_i \left( \frac{X}{d} \right) \cdot \sum_{n=1}^{\infty} \left[ \frac{2C_o}{n \pi} \exp \left( -D_A \cdot t \left( \frac{n \pi}{d} \right)^2 \right) \sin \left( \frac{n \pi X}{d} \right) \right]$$

(3.9)

where $d$ is the thickness of the soil specimen and $D_A$ is the apparent diffusion coefficient at steady-state. By integrating the flux at $X=d$, the amount of species diffused through the clay specimen can be determined from the following equation:

$$\frac{Q}{A \cdot d \cdot C_o} = \frac{D_A \cdot t}{d^2} - \frac{1}{6} \cdot \sum_{n=1}^{\infty} \left[ \frac{(-1)^n}{n^2} \cdot \exp \left( \frac{D_A \cdot (n \pi)^2 \cdot t}{d^2} \right) \right]$$

(3.10)

where $A$ is the area of the specimen. As $t \to \infty$, the above equation reduces to:

$$q = \frac{Q}{A} = C_o \cdot D_A \cdot \frac{t}{d} - C_o \cdot \frac{d}{6}$$

(3.11)

the slope of the above equation is $\left( \frac{C_o \cdot D_A}{d} \right)$ and intercepts the time axis at a time lag, $t_c$, equal to:

78
\[ t_e = \frac{d^2}{6 D_A} \quad (3.12) \]

as shown in Figure 3.4.

3.3 Summary

Different types of methods often used in the laboratory to measure the apparent diffusion coefficients at steady-state, \( D'_A \), and at transient-state, \( D_A \), were presented and deeply examined. The advantages and the disadvantages of each of these methods were discussed and their applicability to soil were outlined. In-diffusion methods can be used to obtain the high and the average pore diffusivity by varying the diffusion time; whereas, the through-diffusion method used to determine the mobility of the absorbed species and the amount of water available for diffusion. For clear understanding of the diffusion process, the through-diffusion method must be supplemented by in-diffusion methods.
Figure 3.4 Schematic diagram illustrating the cumulative flux $q$, vs. diffusion time $T$, curve and its related parameters.
CHAPTER 4

Free-Water Model

It has been mentioned previously that clay minerals are being increasingly used as a sealing material in the engineering design of waste disposal sites to limit and inhibit the migration of contaminants to the surrounding environment. It was also mentioned that the principle mechanism of contaminants to transport through these materials is dominated by diffusion. Thus, the diffusion coefficients are critical parameters for predicting migration rates and fluxes, and for assessing the safety of the disposal sites.

Several methods have been developed to measure and predict the diffusion coefficients, such as those discussed in the previous chapter, but these methods are found to be expensive and very time consuming. The diffusion coefficients are found to depend on several factors, such as: type of diffusing species, clay density and type, and other environmental factors, like temperature, groundwater chemistry (Cheung et al. 1989). Because of the large number of species, the changing environmental factors, the different clay types generally encountered in the field, and the long time required to determine the diffusion coefficient, it is not feasible to cover the whole range of diffusion coefficients
required. Hence, developing a mathematical model that is capable to predict the diffusion coefficient based on simple parameters is needed.

The free-water model was used by several researchers and investigators to predict the diffusion coefficients of a number of contaminants through different types of systems. For example, Gillham et al. (1984) used the free-water model to predict the diffusion coefficients of species passing through a loose mixture of clay and sand. They found that the predicted and the measured values are in a reasonable agreement. On the other hand, the free-water model failed to predict the diffusion coefficients of contaminants passing through compacted clay soil. Therefore, there was a need to develop a model that can predict the migration of contaminants through this type of soil. As a result, the free-water model was first modified by Cheung et al. 1989. The new model is named the clay-water-interaction model. This model showed a better predicted values of these coefficient in clay soil. The free-water model is discussed first and the clay-water-interaction model will then be discussed in chapter 5.

4.1 Free-water model

The most fundamental coefficient that describes the diffusion of species in free solution is the free-solution diffusion coefficient. This coefficient links the steady-state diffusive flux, $J_r$, to the concentration in free water, $\nabla C_r$, by using Fick's first law as follows:
\[ J_f = -D_o \nabla C_f \] (4.1)

In porous media, contaminants diffuse at a slower rate than those in free-solution because the diffusive pathways are longer and the cross sectional area available for diffusion is smaller. This is due to the presence of the solid matrix in the free solution (as discussed in chapter 2). Therefore, the above equation needs to be modified to account for this reduction in the diffusion coefficients. By using Fick’s first law as a base, the diffusive flux in the pore water per unit surface area of soil, \( J_s \), instead of the diffusive flux per unit surface area of bulk water, \( J_f \), is linked to the concentration gradient of such contaminant species by using the following relation:

\[ J_s = -D_p \theta \nabla C_f \] (4.2)

where \( D_p \) is the pore diffusion coefficient, \( \theta \) is the water saturated porosity which accounts for the reduced cross sectional area of flow, \( \nabla C_f \) is the concentration gradient of the diffusing species. The pore diffusion coefficient \( D_p \) can be expressed as a function of the free-solution diffusion coefficient, \( D_o \), and the tortuosity factor, \( \tau \), by using the following relation:

\[ D_p = D_o \tau \] (4.3)
where \( \tau \) is the tortuosity factor which accounts for the effect of tortuous diffusive pathway.

By assuming that the sorbed species are immobile, the time dependent equation used to describe the diffusion process is the result of the combination of a mass balance equation and of a tracer flux equation, and it is described by the following relation (Gillham et al. 1984):

\[
\theta \frac{\partial C}{\partial t} + \gamma_d \frac{\partial S}{\partial t} = \nabla \left( D_p \theta \nabla C_f \right) \tag{4.4}
\]

where \( \gamma_d \) is the dry density of soil, and \( S \) is the amount of species that has been sorbed or settled per unit mass of dry soil. In the free-water model, the species sorption process is assumed to occur instantaneously. Thus, the relation between the amount of sorbed species and the concentration of such species can be assumed to be linear. The linear sorption process can be expressed as:

\[
S = K_d \ C_f \tag{4.5}
\]

where \( C_f \) is the equilibrium or the final concentration of the species and \( K_d \) is the distribution coefficient. The distribution coefficient, \( K_d \), is defined as the ratio of the amount of sorbed species per unit mass of dry soil to the concentration of species
remaining in the solution, $C_f$. The assumption of Equation 4.5 is valid only if (Gillham et al. 1984):

1. the reaction is instantaneous.

2. sorption process is a function of concentration only; that is, other factors that may affect the diffusion process remains unchanged in the course of the reaction.

3. the sorption process is a linear function of the concentration, that is the distribution coefficient, $K_d$, is constant.

4. the sorption process is a unique function of concentration; that is, the reaction is fully reversible and non-hysteretic.

Substituting Equation 4.5 into Equation 4.4 and dividing both sides by $\theta$, the time dependent equation can be reduced to:

$$\frac{\partial C_f}{\partial t} + \frac{K_d \gamma_d}{\theta} \frac{\partial C_f}{\partial t} = \nabla (D_p \nabla C_f) \tag{4.6}$$

by using Fick's second law of diffusion as a base, the time dependent equation can be written as:

$$\frac{\partial C}{\partial t} = D_A \frac{\partial^2 C}{\partial X^2} \tag{4.7}$$

where $D_A$ is the apparent diffusion coefficient of the diffusing species and it is related to the pore diffusion coefficient, $D_p$, as follow:
\[ D_A = \frac{D_p}{1 + \frac{K_d \gamma_d}{\theta}} \]  

Equation 4.8

The apparent diffusion coefficient in Equation 4.8 has been retarded by the term 
\[ 1 + \frac{K_d \gamma_d}{\theta} \], which is known as the retardation factor and it is denoted by the symbol \( R \).

Clay water system in this model is treated as a free-water and the diffusion process occurs in the free-water only. The tortuosity factor in this model can be assumed to be equal to the porosity \( \theta \) for some type of soils (Manheim, 1970). By using the Free-water model, the measured apparent diffusion coefficients obtained from the previously discussed methods, i.e. in-diffusion and through-diffusion, can be interpreted by Equation 4.2 and Equation 4.7 as follows:

\[ D_A = \frac{D_p}{R} \]  

Equation 4.9

and

\[ D'_A = D_p \theta \]  

Equation 4.10

The free-water model assumes the following:

1) The sorption process is assumed to occur instantaneously.

2) The sorbed species are assumed to be immobile.

3) Interstitial water is treated as free-water.

4) The diffusion of the contaminant species occur in the free water only.
In order for the free-water model to be valid the following experimental results would be expected:

1) \( D_A \) does not depend on diffusion time and initial concentration, since sorption is assumed to be constant and the interstitial water is treated as free water.

2) \( D_A \) should be smaller for species with greater \( K_d \), i.e. \( D_A \) for cations is greater than that for anions.

3) The ratio of \( D'_A / D_A \) for non sorbed species, i.e. anions, should be equal to \( \theta \) according to Equations 4.9 and 4.10.

4) \( D'_A \) should be the same for both cations and anions, for species having the same \( D_n \), since \( \tau = \theta \).

### 4.2 Application of Model to Soil

The apparent diffusion coefficient at steady-state, \( D'_A \), and at transient-state, \( D_A \), have been measured by several studies and experiments. Most of these studies and experiments interpreted their results based on the free-water model. The free-water model is found to be valid for sandy soil and for loose non-active cohesive soil, like Kaolinite. However, for compacted active cohesive soil, like montmorillonite\(^8\), the free water model is not valid as illustrated by the following results.

---

\(^8\)For a thorough information about the main type of clay mineral the reader is referred to appendix C.
Microstructure studies on several soil materials showed that heterogeneous diffusion may occur, i.e. the apparent diffusion coefficients may vary with time as shown in Figure 4.1 and Figure 4.2. Figure 4.1 shows the relation between the apparent diffusion coefficients and the diffusion time period in similar compacted clay specimens for different types of diffusing species (Cheung et al. 1989, Oscarson et al. 1993, Cho et al. 1993). The values of the apparent diffusion coefficients are found to decrease as the diffusion time increases. This indicates that $D_A$ is a time dependent parameter and heterogeneous diffusion does occur in the diffusion process. Similar findings have been reported by Lai (1967) and Torstenfelt 1986. The results obtained from Lai are presented in Figure 4.2. Figure 4.2 shows that the apparent diffusion coefficients, $D_A$, for both Sodium, Na\(^+\), and Potassium, K\(^-\), in saturated Kaolinite have not changed with time; whereas, the apparent diffusion coefficients, $D_A$, for the same species in saturated bentonite have been decreased with time. However, the variation of $D_A$ with time is not clear and further studies are required. The results obtained from Figure 4.1 and Figure 4.2 indicates that heterogeneous diffusion does occur, i.e. the apparent diffusion coefficients are time dependent parameters. This result does not agree with the first expected result.

Several diffusion studies and experiments have been performed using the through-diffusion test (Cheung et al. 1989, Oscarson et al. 1992). Some of these studies showed that the apparent diffusion coefficient at steady-state, $D'_A$, for cations are greater than those for anions. Table 4.1 presents some of the results obtained from experiments performed on Na-montmorillonite. These results did not agree with the third and the
Figure 4.1 Relationship between apparent diffusion coefficient $D_A$ and diffusion time $T$ for Cesium Cs\(^+\), Strontium Sr\(^2-\), and Iodine I\(^-\) through Avonlea Bentonite at $\gamma_o=1.75$ Mg/m\(^3\)  
Figure 4.2  Relationship between apparent diffusion coefficient $D_A$ and diffusion time $T$ for Potassium $K^-$ and Sodium $Na^+$ through Kaolinite and Bentonite at $\gamma_c=1.75\text{Mg/m}^3$ (Lai 1967)
fourth assumption.

Table 4.1 also shows that the measured values of $D'_A$ for Cs are much greater than those of $I'$ and $Cl'$. This result does not agree with the fourth expected result. In addition to that, the significant change in the measured values of $D'_A$ for Cs indicates that the diffusing species could be mobile. This result does not agree with the second assumption.

4.3 Summary

The free-water model was introduced and discussed in this chapter. This model was found to be suitable for sandy soil but for the case of clay soil and especially compacted clay this model was found to be inadequate. This is because the properties of water due to clay water interaction was not considered. Therefore, there is a need for developing a new model that has the ability to interpret the diffusion results based on clay water species interaction. The new is model named the clay-water-interaction model and is discussed in the following chapter.
Table 4.1 Measured diffusion coefficient $D'_A$ for different types of species and various densities\(^9\)

<table>
<thead>
<tr>
<th></th>
<th>$\gamma_d$</th>
<th>$D'_A \times 10^{-12}$</th>
<th>$K_d$</th>
<th>$K_{dm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg/m(^3)</td>
<td>m(^2)/sec</td>
<td>L/Kg</td>
<td>L/Kg</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>1.25</td>
<td>45.00</td>
<td>21.00</td>
<td>20.00</td>
</tr>
<tr>
<td></td>
<td>1.75</td>
<td>2.00</td>
<td>700.00</td>
<td>3.60</td>
</tr>
<tr>
<td>Cl(^-)</td>
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<td>&lt;0.1 - 1</td>
<td>≈ 0</td>
<td>≈ 0</td>
</tr>
<tr>
<td></td>
<td>1.75</td>
<td>&lt;0.1 - 1</td>
<td>≈ 0</td>
<td>≈ 0</td>
</tr>
<tr>
<td>I(^-)</td>
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<td>&lt;0.1 - 1.5</td>
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</tr>
<tr>
<td></td>
<td>1.75</td>
<td>&lt;0.1 - 0.2</td>
<td>≈ 0</td>
<td>≈ 0</td>
</tr>
</tbody>
</table>

\(^9\) After Cheung et al. (1989)
CHAPTER 5

Clay-Water-Interaction Model

The free-water model was introduced and analyzed in the previous chapter, where it was found to be valid for sandy soil but for clay based materials the model was found not to be valid. Therefore, there is a need to find a new model that has the ability to predict the diffusion coefficients of species migrating through clay based materials. As a result, the clay-water-interaction model was first developed by Cheung et al. (1989). Cheung's model will be further developed below.

5.1 Clay-Water-Interaction Model

In this model, the diffusion of contaminant species in clay is considered to be heterogeneous. Heterogeneous diffusion arises from the electrochemical forces that exist between clay particles, clay water and dissolved species. This results in a non-uniform distribution in ionic concentration and water viscosity around the clay particles (Cheung 1989). The distribution of diffusing species in clay soil depends on the clay-water-species interaction. Clay-species interactions arises from various processes including chemisorption (specific sorption) and ion-exchange (non-specific sorption). In the ion-exchange process, the electrochemical forces between the soil particles and the
diffusing species are generally weak; the adsorbed species may be shared under a driving concentration gradient and thereby become mobile. The ion-exchange interaction depends on the ionic strength of the pore solution: the higher the ionic strength, the less the sorption by ion-exchange of a given species. On the other hand, in the chemisorption process, the forces holding the diffusing species to the soil particles are very strong and they can hardly be mobilized under a driving concentration gradient (Cheung 1993).

Clay particles usually carry a net negative charge on their surface. Therefore, cations are attracted to the surface of the clay, whereas, anions are repelled from the surface of the clay. As a result of this attraction and repulsion process, the ionic concentration gradient along the surface of the clay particles is higher for cations and smaller for anions. The diffusivity flux is found to be directly related to the concentration gradient, i.e. the diffusivity flux increases by increasing the concentration gradient. In addition to that, the viscosity of the solution plays a noticeable role in the diffusion process. The viscosity of the water in the first two layers adjacent to the surface of the clay particles is much higher than the rest of the water, which is not significantly different from the free water (Low 1961, Cheung 1993). The diffusivity flux is found to be inversely related to water viscosity, i.e. the diffusivity flux reduces by increasing water viscosity.
In accordance with its physical and chemical properties, clay water can be classified here into three types: Surface water, Interlayer water and Interstitial water. Surface water, is the first two layers of water ( = 1 nm in thickness ) adjacent to the surface of the clay particle. The properties of this layer are strongly influenced by the properties of the clay particle. Interlayer water is the water that lies beyond the surface water between parallel clay particles. The influence of this layer on the diffusion process is much lower than that of the surface water. This layer is relatively large in loose montmorillonite with low salinity solution, but it is relatively small in highly compacted montmorillonite and in loose montmorillonite with high salinity solution. Interstitial water is the water that lies beyond the interlayer water in large soil pores. It is considered to have similar properties to those of free water ( Low 1961, Cheung et al. 1989 ). For the purpose of this model, surface and interstitial water are the only types considered. This is because interlayer water has little effect on the diffusion process. Thus, this layer can be neglected. Figure 5.1 is a diagram that illustrates the types of water in the clay-water-interaction model.

The diffusive flux for the two types of clay water is given by the following relation:

\[
J_s = -(D_{pf} \theta_f \nabla C_f + D_{ps} \theta_s \nabla C_s)
\]  \hspace{1cm} (5.1)

where \( J_s \) is the steady state flux in the pore water per unit surface area of the soil, \( D_{pf} \) and \( D_{ps} \) are the pore diffusion coefficients of contaminant species in the interstitial and surface
water respectively, \( \theta_i \) and \( \theta_s \) are the fractional volume of water for interstitial and surface water respectively, and \( \nabla C_i \) and \( \nabla C_s \) are the ionic concentration for each type of water interstitial and surface water.

Assuming:

\[
C_s = \frac{K_d \gamma_d \delta_s}{\theta} C_f
\]  

(5.2)

where \( \delta_s \) is the fraction of the surface water that is available for diffusion to account for the size factor of the surface pore and the diffusive species, and \( K_d \) is the distribution coefficient. Equation 5.1 can then be written as:

\[
J_s = -(D_{pf} \theta_f \delta_f + D_{ps} K_d \gamma_d \delta_s) \nabla C_f
\]  

(5.3)

In the development of the above equation, the diffusion in each type of water is assumed to be isotropic and isothermal and the pores are assumed to be interconnected. For small diffusing species \( \delta_i \) can be taken as 1, as the interstitial water are relatively large. However, for large diffusing species, some of the interstitial water may not be large enough to allow the species to penetrate through. Thus, \( \delta_i \) needs to be investigated. Equation 5.3 shows that for \( \delta_s = 0 \), the predominant diffusion pathway for cations and anions is expected to be in the interstitial water, where as, for large values of \( \delta_s \) the predominant diffusion pathways is expected to be dependent on the charge of the diffusing
species. It also shows that the predominant diffusion pathway for cations such as Cs\(^+\) and Sr\(^+\) (where \(K_d >> 1\)) is expected to be in the surface water because of the attraction forces that exist between the cations and the clay particles. On the other hand, the diffusion pathway for anions (\(K_d = 0\)), such as Cl\(^-\) and I\(^-\), is expected to be in the interstitial water because of the repulsion forces that exist between the anions and the clay particles.

If the dominant diffusion pathway for small species is considered to be in interstitial water, which is the case of anions and cations with a value of \(\delta_s = 0\), the diffusive flux \(J_s\) will become:

\[
J_s = -D_f \Theta_f \nabla C_f \quad (5.4)
\]

and

\[
D_f = D_o \tau_f \quad (5.5)
\]

where \(\tau_f\) is the tortuosity factor in the interstitial water. The time dependent equation derived from Equation 5.4 can be written as:

- For non sorbed species (\(K_d = 0\))

\[
\frac{\partial C_f}{\partial t} = D_f \nabla^2 C_f \quad (5.6)
\]

- For immobile sorbed species (\(K_d > 0\))

\[
\frac{\partial C_f}{\partial t} = \frac{D_f}{1 + \frac{K_d \gamma_d}{\theta}} \nabla^2 C_f \quad (5.7)
\]

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In Equation 5.7 the value of $D_A$ is retarded by a factor of $1 + \frac{K_d \gamma_d}{\theta}$, known as the retardation factor. This retardation process occurs due to the transfer of ions from the interstitial water to the surface water. Theoretically, the retardation factor is expected to depend on the diffusion time and the distribution of the interstitial water. Therefore, this factor is expected to be large for longer diffusion times and for uniform distribution of interstitial water. However, for short diffusion time the retardation factor can be neglected, since the transfer is very small.

For non-reactive species such as $I^-$ ($K_d = 0$), the measured apparent diffusion coefficients can be interpreted as follows:

$$D_A = D_f$$

and

$$D'_A = D_f \theta_f$$

(5.8)

(5.9)

Figure 5.2 illustrates the effect of anion extrusion that is demonstrated by the ratio of $\theta_r / \theta$. The values of $\theta_r$ can be obtained experimentally by dividing the value of $D'_A$ by $D_A$ ( according to Equation 5.8 and Equation 5.9 ). A value of $\theta_r / \theta < 1$ suggests that anion exclusion plays an important role in the system. The effect of anion exclusion increases as the value of $\theta_r / \theta$ decreases. For the measured values of $\theta_r / \theta$ to be appropriate, the concentration gradient within the clay plug obtained from the
through-diffusion experiment must be linear. Furthermore, the measured value of $\frac{\Theta_r}{\theta}$ should be equal to the ratio of the bulk concentration, $C$, to the source reservoir concentration, $C_0$, at the interface on the clay plug and the source reservoir.

If the dominant diffusion pathway is considered to be in surface water, which is the case for cations and neutral species, where $\theta$, $\delta_s$ is much greater than $\theta_r$, the diffusive flux can be written as:

$$J_s = -D_s \theta_s \delta_s \nabla C_s$$ (5.10)

and

$$D_s = D_o \tau_s \mu_s$$ (5.11)

where $\mu_s$ is the viscosity of the pore solution in the surface water, and $\tau$, is the tortuosity factor in the surface water. In Equation 5.11, the upper and the lower values of the viscosity $\mu$, are 0.2 and 0.9 respectively (Cheung 1993). The value of $\delta_s$ in Equation 5.10 can be estimated from the bulk concentration profile after performing the through-diffusion experiment. Since the steady state condition is established in this experiment, the bulk concentration, $C$, can be approximated by $\delta_s (\theta + K_d \gamma_d) C_r$. For adsorbed species $K_d$ is much greater than $\theta$, thus, the bulk concentration, $C$, can be further approximated by $\delta_s K_d \gamma_d C_r$. Since $C_r$ is equal to $C_0$, the source reservoir concentration at the interface of the clay plug and the source reservoir, $\delta_s$ can be calculated from the following relation (Cheung 1993):
\[
\frac{C}{C_0} = \delta_s K_d \gamma_d
\]  \(5.12\)

where \(C/C_0\) is the value obtained from the bulk concentration profile at the interface of the clay plug and the source reservoir. In order for Equation 5.12 to be valid, the bulk concentration profile should be linear.

Since the mobility of the sorbed species depends on the type of interaction that exists between the clay particles and the diffusing species, the mobility of the sorbed species is considered for the following:

- If the sorbed species are considered to be mobile, \(\nabla C_s\) can be related to \(\nabla C_f\) by the following Equation:

\[
\nabla C_s = \frac{K_d \gamma_d}{\theta_s} \nabla C_f
\]  \(5.13\)

Substituting Equation 5.4 for \(\nabla C_s\) into Equation 5.10, the diffusive flux equation will become:

\[
J_s = -D_s \delta_s K_d \gamma_d \nabla C_f
\]  \(5.14\)

where \(K_d \delta_s\) is a factor accounts for the increase in the concentration gradient due to cation exchange of mobile species. The time dependent equation derived from Equation 5.14 can be written as:
\[ \frac{\partial C_f}{\partial t} = D_s \frac{\partial^2 C_f}{\partial x^2} \]  

(5.15)

For this condition, the apparent diffusion coefficients obtained from the previously discussed methods can be interpreted as follows:

\[ D_A = D_s \]  

(5.16)

and

\[ D'_A = D_s \delta_s K_d \gamma_d \]  

(5.17)

If all the adsorbed species are mobile, then the following results are expected:

1) The \( D_s \) value obtained from the measured \( D'_A \) should be equal to the measured \( D_A \), according to Equation 5.16 and Equation 5.17.

2) The measured \( D'_A \) value for cations should be greater than that of anions, \( \theta_s \) is much greater than \( \theta_f \) in compacted clay materials.

- If the adsorbed species are considered to be immobile, \( \nabla C_s \) is equal to \( \nabla C_f \) since the gradient of the sorbed species in the surface water does not contribute to the diffusion process. The diffusive flux can be written as:

\[ J_s = - D_s \theta_s \delta_s \nabla C_f \]  

(5.18)
and the time dependent equation derive from Equation 5.18 can be written as:

\[
\frac{\partial C_f}{\partial t} = \frac{D_s}{1 + \frac{K_d \gamma_d}{\theta}} \frac{\partial^2 C_f}{\partial X^2}
\]  

(5.19)

For this condition, the apparent diffusion coefficients obtained from the previously discussed methods can be interpreted as follows:

\[
D_A = \frac{D_s}{R}
\]  

(5.20)

and

\[
D'_A = D_s \theta_s \delta_s
\]  

(5.21)

For the clay-water-interaction model to be valid the following results are expected:

1) \(D_A\) may vary with time

2) \(D_A\) depends on the predominant diffusion pathway, charge of species, soil fabric, diffusion time, and initial concentration.

3) \(D_A\) can be smaller for cations than anions due to higher viscosity.

4) \(D_A\) for mobile cations should not be affected by the \(K_d\) value.

5) \(D'_A\) for mobile cations can be greater than that of anions.

6) When \(D_s = \frac{F_s}{\theta_s \delta_s K_d \gamma_d V C_f}\) is constant, then this spieces is mobile.
Figure 5.1 Schematic diagram illustrate the interstitial and surface water in clay

Figure 5.2 Diagram illustrate the effect of anion exclusion
5.3 Summary

A model that can predict the diffusion coefficients of contaminants migrating through clay based materials has been developed and termed the clay-water-interaction model. The apparent diffusion coefficients obtained showed to be dependent on clay type, clay density, type of contaminant species, and other environmental conditions, like temperature, groundwater chemistry, density of the underlying materials, and the mobility of contaminants. A parametric analysis for selected parameters are proceeded to study the extent of the effect of these parameters on the diffusion coefficient. These analysis are discussed in the following chapter.
CHAPTER 6

Parametric Analysis and Relationship

The measured diffusion coefficients are found to be dependent on clay density and structure, clay type, and other environmental factor such as pH level, temperature, chemistry of the solution etc. The effect of these factors on the diffusion process can be assessed by studying each of them separately. A parametric analysis of some of these factors which directly effect the diffusion process are discussed in the following sections.

6.1 Clay Density

Clay density affects the apparent diffusion coefficient in two main parts. The first part remains in the effect of clay density on the pore magnitude and size. As the density of a soil sample increases the pore size decreases, hence the apparent diffusion coefficient reduces. This reduction in the $D_A$ value occurred because many species with hydrated radius greater than the pore size can no longer pass through, thus this process acts as a sinking source. Because there is no single method available to predict the size of the pores between soil particles, this part has not been discussed in this study. The second part remains in the effect of clay density on the tortuosity factor, i.e. the length of the diffusion pathway. As the clay density changes, the diffusion path-length will also changes, hence,
the apparent diffusion coefficient is altered by these changes. A detailed analysis of the effect of the clay density on the tortuosity factor is proceeded in the following section.

6.1.1 Tortuosity Factor

The tortuosity factor can be experimentally calculated for anions by dividing the apparent diffusion coefficient \( D_A \) by the free-solution diffusion coefficient \( D_o \) and the viscosity factor \( f_v \); it is expressed as follows:

\[
\tau = \frac{D_A}{D_o f_v}
\]  

(6.1)

Some of the selected values of the experimental apparent diffusion coefficients obtained from literature, their free-solution diffusion coefficient \( D_o \) and the calculated tortuosity factor are presented in Table 6.1. The range of the \( \tau \) values listed in Table 6.1 is highly variable but it is always less than one.

Several researchers have related the apparent diffusion coefficient with the volumetric moisture content, i.e. the porosity of the soil. For example, Manheim (1970) and Lerman (1978) assumed the following relationship to be valid between the apparent diffusion coefficient \( D_A \) and the total porosity of the soil \( \theta \):

\[
D_A = D_o \theta^n
\]  

(6.2)


\(^{10}\) Viscosity factor discussed in a later section.
This suggests that the tortuosity factor can be represented by the total porosity. Based on the results obtained from plotting the values of $D_A$ for NaCl versus the corresponding $\theta$ on a log-log scale, the exponent $n$ is best estimated to be equal to 2, Shackelford (1989).

Others, such as Myrand et al. (1987) reported that Desaulniers (1986) found the following relation to be valid for diffusion in saturated, unconsolidated fine-grained geologic materials:

$$D_A = D_o n^2 \quad (6.3)$$

where $n$ is the total porosity of the soil. For saturated soil $\theta = n$, hence the assumption of Desaulniers (1986) agree with those of Manheim (1970) and Lerman (1978).

This study represents the tortuosity factor by another factor termed the effective porosity, which is related to the porosity of the soil but less in magnitude than the total porosity. The total porosity term was defined in many soil mechanics text books as the ratio of the volume of voids over the total volume of the soil. For fully saturated soil this term can be expressed as:

$$\theta = \theta_s + \theta_f \quad (6.4)$$

where $\theta = \text{total volume of water and is referred to as the total porosity.}$
\[ \theta_s = \text{total volume of surface water and is referred to as the surface porosity.} \]

\[ \theta_f = \text{total volume of interstitial water and is referred to as the free porosity.} \]

Experimentally it was found that not all of the above volumes are available for diffusion, this is related here to the presence of dead-end pore volume. The dead-end pore volume defined here as the volume which contains the diffusing species and acts as a source of sink during transient diffusion; these pores could be cavities (i.e. pores with only one opening) and/or small pore size compared to the size of the diffusing species. As a result, the effective porosity is used here instead of the total porosity.

Assuming a unit volume, the effective porosity can be estimated as follows:

For species diffusing in interstitial water, the total porosity is equal to the dead-end pore volume plus the free porosity; and Figure 6.1 illustrates this. The following calculation proceeds with reference to Figure 6.1:

\[ \frac{\theta_{\text{dead-end}}}{\theta} = 1 - \theta_f \]

thus

\[ \theta_{\text{dead-end}} = (1 - \theta_f) \theta \]

Since the species are diffusing in the interstitial water, the surface water pore volume should be excluded. Hence, the dead-free pore volume in interstitial water is equal to:

\[ \theta_{\text{dead-free}} = \left\{ (1 - \theta_f) \theta \right\} - \theta_s \]
since \[ \theta_r = \theta_{ef} + \theta_{\text{dead-free}} \]

thus, the effective free porosity can be calculated from:

\[
\theta_{ef} = \theta_r - \{[(1 - \theta_r) \theta ] - \theta_s \}
\]

\[
= \theta_r - [(1 - \theta_r) \theta ] + \theta_s
\]

Substituting Equation 6.4 into the above equation, the effective porosity can be written as:

\[
\theta_{ef} = \theta_r * \theta
\]  \hspace{1cm} (6.5)

For species diffusing in surface water, the porosity will be equal to the dead-end pore volume plus the surface water pore volume; and Figure 6.2 illustrates this. The calculation proceeds in a similar manner to that of the interstitial water. Hence, the effective surface porosity can be estimated from:

\[
\theta_{cs} = \theta_s * \theta
\]  \hspace{1cm} (6.6)
Figure 6.1 Diagram illustrates pore volume distributions for species diffusing in interstitial water per unit volume.

Figure 6.2 Diagram illustrates pore volume distributions for species diffusing in surface water per unit volume.
6.1.2 Comparison with Literature

A comparison between the measured apparent diffusion coefficients obtained from literature and those calculated according to the previous hypothesis are presented in Table 6.1 for anions and Table 6.2 for cations. The data shown in Table 6.1 indicates that the calculated value of $D_A$ using $\tau = \theta_{ef}$ are in better agreement with the measured values than those using $\tau = \Theta$. This is also illustrated in Figure 6.3 and Figure 6.4. In addition, a comparison between the measured tortuosity factor and the total and the effective porosity was also made in this study. Table 6.1 also shows that, for compacted clay, the calculated tortuosity factors base on Equation 6.1 are better represented by $\theta_{ef}$ than by $\Theta$, see Figure 6.5 and Figure 6.6. On the other hand, for the case of sandy soil and loose clay $\tau$ is better represented by $\theta_{bulk}$, see section 6.2.

Another point should also be considered when calculating $D_A$, is the thickness of the double layer (surface water). A better relation noticed between the measured and the calculated $D_A$ when assuming the thickness of the double layer at a clay density less than 1.25 Mg/m$^3$ to be equal to 5 Å (two layers)\textsuperscript{11}, and at clay density greater than 1.25 Mg/m$^3$ to be equal to 2.5 Å (one layer). This relation is illustrated in Figure 6.7 and Figure 6.8. Further investigations and experiments in estimating the thickness of the double layer is required.

\textsuperscript{11} The thickness of a single liquid layer is assumed to be approximately equal to 2.5 Å.
In case of cations, several variables that effect the diffusion process had to be assumed in order to calculate the value of $D_A$. This is because the literature lacks a detailed analysis of the obtained results for $D_A$ which are required to determine the values of these variables. The calculated values of $D_A$ based on the assumptions made in Table 6.2 show that Cadmium Cd$^{2+}$, Zinc Zn$^+$, and Strontium Sr$^+$ are all diffusing in surface water and they are mobile. The data listed in Table 6.3 also shows a reasonable agreement between the calculated and the measured values of $D_A$. From the above, it is clear that the tortuosity facto $\tau$ is better represented by the effective porosity, $\theta_{es}$. Further investigations and detailed experiments are required to validate this hypothesis and to model the assumed variables. Once this is done, one can easily model the apparent diffusion coefficient for cations.

The effect of anion extrusion should also be considered when studying the diffusion process. Chapter 5 showed that anion extrusion plays an important role in the diffusion process. This effect can be demonstrated by dividing the experimental value of $\theta_r$ by the total porosity $\theta$. Selected values of $\theta_r$ and $\theta_r/\theta$ (obtained from literature) are presented in Table 6.3. The values of $\theta_r/\theta$ are found to be decrease as the density of clay increases. The smaller values of $\theta_r/\theta$ indicates a greater effect of anion extrusion on the diffusion process. Furthermore, the measured values of some of the $\theta_r/\theta$ are found to be similar to those of $C/C_0$ (the concentration value obtained from the bulk concentration profile at the interface of the clay plug and the source reservoir) and the concentration profile for those experiments are found to be linear. These results prove the validation of
the anion extrusion. The effect of anion extrusion has also been demonstrated here by the estimated value of $\theta_{ae} / \theta$. A reasonable agreement between the experimentally measured $\theta_{e} / \theta$ and the calculated $\theta_{ae} / \theta$ is found, see Table 6.3 and Figure 6.9. This indicates that the effect of anion extrusion can be estimated by $\theta_{ae} / \theta$.

In conclusion, the study found that the assumption of $\tau = \theta_{\text{effective}}$ and the thickness of the double layer to be equal to 2.5 Å at clay density greater than 1.25 Mg/m$^3$ and equal to 5 Å at clay density less than 1.25 Mg/m$^3$ resulted in better predicted values of $D_{\lambda}$ when compared to the measured values.

![Figure 6.3 Comparison between the measured and the calculated $D_{\lambda}$ values for Iodine](image)
Figure 6.4 Comparison between the measured and the calculated $D_a$ values for Chlorine

Figure 6.5 Comparison between the measured and the calculated tortuosity factor for Iodine
Figure 6.6 Comparison between the measured and the calculated tortuosity factor for Chlorine

Figure 6.7 Effect of the diffuse double have been included in the comparison between the measured and the calculated value of $D_A$ for Iodine
Figure 6.8 Effect of the diffuse double have been included in the comparison between the measured and the calculated value of $D_a$ for Chlorine

Figure 6.9 Effect of clay density on anion extrusion
Table 6.1  Comparison between the measured and the calculated diffusion coefficient $D_A$ for anions at different clay densities

<table>
<thead>
<tr>
<th>Species</th>
<th>Clay Density Mg/m$^3$</th>
<th>Surface Area m$^2$/g</th>
<th>$D_A$ (measured) m$^2$/sec</th>
<th>$\tau$ (measured)</th>
<th>$\theta$</th>
<th>$\theta_s$</th>
<th>$\theta_f$</th>
<th>$\theta_{ef}$</th>
<th>$D_A$ (calc.) ($\tau = \theta$) m$^2$/sec</th>
<th>$D_A$ (calc.) ($\tau = \theta_{ef}$) m$^2$/sec</th>
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<td>I</td>
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Table 6.2  Comparison between the measured and the calculated diffusion coefficient $D_A$ for cations at different clay densities

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<th>$D_A$ (measured) (m$^2$/sec)</th>
<th>$R$</th>
<th>$\Theta$</th>
<th>$\Theta_s$</th>
<th>$\Theta_f$</th>
<th>$\Theta_{es}$</th>
<th>$D_A$ (calc.) ($\mu=0.2$ &amp; mobile) (m$^2$/sec)</th>
<th>$D_A$ (calc.) ($\mu=0.9$ &amp; mobile) (m$^2$/sec)</th>
<th>$D_A$ (calc.) ($\mu=0.2$ &amp; immobile) (m$^2$/sec)</th>
<th>$D_A$ (calc.) ($\mu=0.9$ &amp; immobile) (m$^2$/sec)</th>
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<td>0.33</td>
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### Table 6.3 The effect of bentonite density on anion exclusion

<table>
<thead>
<tr>
<th>Species</th>
<th>Clay Density Mg/m³</th>
<th>( D'_A ) (mes.) ( \text{m}^2/\text{sec} )</th>
<th>( D_A ) (mes.) ( \text{m}^2/\text{sec} )</th>
<th>( C/C_o ) (mes.)</th>
<th>( D'_A/D_A/\theta )</th>
<th>( \theta )</th>
<th>( \theta_s )</th>
<th>( \theta_f )</th>
<th>( \theta_{ef} )</th>
<th>( \theta_{ef}/\theta )</th>
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<td>0.440</td>
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<td>0.590</td>
<td>0.260</td>
<td>0.330</td>
<td>0.200</td>
<td>0.330</td>
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<tr>
<td></td>
<td>1.09</td>
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<td>0.590</td>
<td>0.260</td>
<td>0.330</td>
<td>0.190</td>
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<td>0.180</td>
<td>0.070</td>
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6.2 Clay Content

In the previous section it was mentioned that the geometry of the soil sample greatly affects the apparent diffusion coefficient values. The literature contains several diffusion studies and experiments that were performed on different clay to sand ratios. The data presented by Gillham et al. and others illustrates the effect of the clay content on the apparent diffusion coefficient is listed in Table 6.4 and in Table 6.5. Gillham et al. (1984) performed a series of diffusion experiments on seven mixtures of bentonite and silica sand ranging from 0 to 100 percent of bentonite by weight. The results of their experiments demonstrated that the porosity and the bulk density considerably influenced the measured apparent diffusion coefficients. They also suggested that a small amount of bentonite ranging between 5 to 10 percent mixed with sand was found to be more effective in retarding contaminants or diffusing species than either sand alone or sand-bentonite mixtures containing a large portion of clay (see Figure 6.10 and Figure 6.11). They commented that, at this range of sand-bentonite mixture (5 - 10 %) all the pores between the sand particles are almost completely filled by the clay particles. Thus the porosity term reached its minimum value at this range of clay content (5 - 10% sand-bentonite mixture), as shown in Figure 6.12. This would be true if nonreactive soil such as sand or a soil sample that contains a large percentage of sand, or loss cohesive soil was used, hence, the porosity would be the main factor that influences the measured value of $D_A$. Since clay minerals are always active, sand particles will only act as a filler. Therefore, it is expected that the apparent diffusion coefficient is considerably influenced by the clay content portion rather than the sand content.
In order to study the effect of the clay content on the apparent diffusion coefficient, a comparison between the measured values of $D_A$ and the calculated values depending on the bulk density and the clay density was performed. The measured values of $D_A$ obtained from literature and the calculated values are listed in Table 6.4 for anions and Table 6.5 for cations. The data presented in Table 6.4 shows that the measured apparent diffusion coefficient at high sand content are better represented by using the bulk density; whereas, at low sand content $D_A$ values are better represented by using the clay density (with the exception of iodine). In case of iodine, it is expected that either a mistake occurred during the measurement of $D_A$ or some variables which effect $D_A$ were not noted or detected (such as the organic content in the soil). In case of cations, the calculated values of $D_A$ based on the assumption listed in Table 6.5 shows that Strontium $\text{Sr}^{2+}$ diffuses in surface water and is mobile. The data presented in Table 6.5 also shows that the measured apparent diffusion coefficient values at high sand content are better represented by using the bulk density as a base; whereas, at low sand content $D_A$ values are better represented by using the clay density as a base.

In conclusion, the clay density should always be used as a base when attempting to model the migration of contaminants through compacted active materials, such as clay, and the bulk density might be used when attempting to model the migration of contaminants through loose nonreactive materials, such as sand. In case of loose active materials further studies are needed.
Figure 6.10  Comparison between the measured and the calculated $D_A$ values based on bulk density and clay density for Cl
Figure 6.11 Comparison between the measured and the calculated $D_a$ values based on bulk density and clay density for H-3.

Figure 6.12 Effect of Bentonite-Sand mixture on the measured tortuosity factor for both Cl and H-3.
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<th>% of bentonite</th>
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<th>$D_A$ (mes.) m$^2$/sec</th>
<th>$\tau$ (mes.)</th>
<th>Clay Density Mg/m$^3$</th>
<th>$\theta$</th>
<th>$\theta_s$</th>
<th>$\theta_f$</th>
<th>$\theta_{ef}$</th>
<th>$D_A$ (cal.) ${\tau=\theta_{ef}}$ m$^2$/sec</th>
<th>$D_A$ (cal.) ${\tau=\theta_{\infty}}$ m$^2$/sec</th>
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6.3 Clay Type

The previous section showed that the tortuosity factor can be represented by the effective porosity, i.e. the geometry of the soil sample. Hence, soil properties are expected to have a considerable effect on the rate of diffusion of contaminant species. Table 6.6 presents experimental results obtained from literature for different types of clay soil and different types of diffusing species. A single relation between the apparent diffusion coefficient and the type of soil could not been found due to the fact that there are a number of variables acting simultaneously which effect the measured values of $D_A$. For the given ions and soil types, the measured $D_A$ values listed in Table 6.6 are found to be inversely related to the specific surface area, i.e. the apparent diffusion coefficient increases as the specific surface area of a soil sample decreases (where other variables are held constant). The relation between the specific surface area and the apparent diffusion coefficient can be explained as follows: in case of anions, as the specific surface area increases the thickness of the surface water increases, thus, the effective porosity $\theta_{ef}$ in the interstitial water decreases. This reduction in $\theta_{ef}$ means that the diffusion pathway for anions increases. Thus, the tortuosity factor decreases. As a result, the apparent diffusion coefficient $D_A$ value decreases. In case of cations, as the specific surface area increases the surface water available for diffusion increases. This means that more species will have the probability to be sorbed on the surface of the clay particles, i.e. the adsorption coefficient factor $K_d$ increases. Depending on whether the species diffusing through surface water are
mobile or immobile, the apparent diffusion coefficient will either increase or decrease, see chapter 5.

A comparison between the measured and the calculated values of $D_A$ are presented in Table 6.6. In case of anions, a reasonable agreement was found between the measured and the calculated values of $D_A$ for all types of clay, with the exception of Lake Agassiz clay. The presence of a large amount of organic content in Lake Agassiz clay resulted in the adsorption of the diffusing anions, this process acted as a sinking source. As a result of this sorption, the measured value of $D_A$ in Lake Agassiz clay was much smaller than the calculated $D_A$. In case of cations, the effect of specific surface area on the diffusion process is clear. Cations diffusing in clay having a small specific surface area, like Kaolinite, are found to diffuse in interstitial water; this is because the surface water is not thick enough to allow cation species to pass through. On the other hand, cations diffusing in clay having a large specific surface area, like Lufkin, are found to be mobile and diffusing in the surface water. This is because the thickness of the surface water is greater, hence, more species are allowed to pass through. This clearly explains the points made in the previous paragraph.

Intensive studies and experiments are required in order to thoroughly understand the effect of clay type on the diffusing species. Once this is done a reasonable relation between the clay type and the apparent diffusion coefficient can be found.
Table 6.6 Effect of clay type on the measured and the calculated values of $D_A$ for both cations and anions

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<th>pH</th>
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6.4 Temperature

The effect of temperature on the apparent diffusion coefficient attracted the attention of a number of researchers since the early stages of diffusion study. In 1965 Gardner mentioned that the diffusion coefficient for anions may vary with temperature, but there was no data to support this statement at that time. In recent literature, a large percentage of diffusion experiments were performed at 25°C (Cheung et al. 1989, Oscarson et al. 1992, Cho et al. 1993 and Gillham et al. 1984). Some experiments were also performed at different elevated temperatures (Robin et al. 1987).

The effect of temperature on the apparent diffusion coefficient should be examined in order to:

1) Determine the effect of temperature on the apparent diffusion coefficient and on soil properties.

2) Find a coefficient which can be used to improve the modeling of the measured apparent diffusion coefficient.

In order to investigate the effect of temperature on the diffusion process, other factors suspected to affect this process must be held constant. Therefore, clay density, ionic strength, type of clay and the concentration of the diffusing species are held constant. Diffusion values were taken from literature at three different elevated temperatures 25°C, 60°C and 90°C. These values are listed in Table 6.7 and Table 6.8.

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The apparent diffusion coefficient is found to be linearly related to the temperature, i.e. the diffusion coefficient increases as the temperature increases. This relation was illustrated in Figure 6.13 to Figure 6.16. The variation between the temperature and the apparent diffusion coefficient is most likely due to:

1) The effect of temperature on the viscosity of the pore solution.

2) The effect of temperature on the geometry of the soil specimen.

3) The effect of temperature on the thickness of the diffuse double layer.

6.4.1 Viscosity

The viscosity of water is known to decrease with increasing temperatures (see appendix A), hence, the apparent diffusion coefficient is inversely linearly related to the viscosity of water (pore solution). Therefore, the viscosity factor is inversely related to the viscosity of the pore solution. The viscosity factor is defined as the viscosity of the pore solution at 25°C divided by the viscosity at the target temperature and it is expressed as follows:

\[ f_v = \frac{\mu_{(25^\circ C)}}{\mu_{(T^\circ C)}} \] (6.7)

where \( f_v \) = viscosity factor.

\( \mu_{(25)} \) = viscosity of the pore solution at 25°C.

\( \mu_{(T)} \) = viscosity of the pore solution at the target temperature.
Hence, the modeling diffusion equation for anions can be modified to:

\[ D_A = D_0 \tau f_v \]  \( (6.8) \)

where \( D_0 \)\(^{12}\) is the free-solution diffusion coefficient at 25°C.

A comparison between the measured apparent diffusion coefficient values obtained from literature and those calculated according to above equation is presented in Table 6.7 and plotted in Figure 6.13 to Figure 6.16. The calculated value of \( D_A \) obtained from Equation 6.8 shows a better agreement with the measured \( D_A \) than those obtained from Equation 5.5. This study models the diffusion process for anions with Equation 6.8 rather than Equation 5.5; this is because Equation 6.8 uses the viscosity of the pore solution when calculating the viscosity factor whereas Equation 5.5 uses the viscosity of the water when calculating the viscosity factor. Further studies and experiments should be performed on different pore solutions to validate Equation 6.8.

In case of cations, a linear relationship was found between the temperature and the apparent diffusion coefficient, i.e. as the temperature increases the apparent diffusion coefficient is also increases (see Table 6.8). This variation is thought to be related to the viscosity of the pore solution. However, a definite relation between the temperature and \( D_o \) values are always taken from literature, and they do not represent the actual value.
the apparent diffusion coefficient could not be achieved at this point because the literature lacks a detail analysis of the obtained results for $D_A$. Thus, several assumptions have to be made in order to calculate $D_A$. The calculated value of $D_A$ based on the assumptions made in section 5.1 shows that Strontium diffuses in surface water and is mobile. The data listed in Table 6.8 also shows a reasonable accordance between the calculated and the measured values of $D_A$. Therefore, it is not necessary to carry out further investigations and analysis to validate this hypothesis. Accordingly, further studies and detailed experiments are required to model these assumed variables; at which point one can draw a clear relation between the temperature and the measured $D_A$.

6.4.2 Soil Geometry

The effect of temperature on the geometry of the soil is also investigated in this section. This is achieved by dividing the measured value of $D_A$ by the free-solution diffusion coefficient $D_o$ and the viscosity factor $f_v$. The relation between the temperature and the geometry of the soil specimen is found to be almost constant, as shown in Figure 6.17. This indicates that the temperature does not have a significant effect on the geometry of the soil.

6.4.3 Diffuse Double Layer

The diffuse double layer is known to be linearly related to the temperature, i.e. the thickness of the double layer increases as the temperature increases (see section 2.1.5).
The data presented in Table 6.7 shows that temperature does not have a significant effect on changing the thickness of the double layer. This can be related to the fact that the clay samples are compacted at high densities (greater than 1.1 Mg/m$^3$). At this density the pore space between particles are extremely small and the double layer is compressed to its maximum and can not easily expand; hence, the temperature has an insignificant effect on changing the thickness of the diffuse double layer.

In conclusion, in compacted clay the temperature mainly affects the viscosity of the pore solution whereas the geometry of the soil specimen and the thickness of the diffuse double layer are not considerably affected by the variation of the temperature. In loose clay further experiments and studies in required.

![Graph](image)

Figure 6.13 Effect of temperature on D$_A$ at 0 ionic strength for Chlorine

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Figure 6.14 Effect of temperature on $D_A$ at 0.27 ionic strength for Chlorine

Figure 6.15 Effect of temperature on $D_A$ at 1.4 ionic strength for Chlorine
Figure 6.16 Effect of temperature on $D_A$ for Iodine

Figure 6.17 Effect of temperature on the geometry of the soil
Table 6.7 Effect of temperature on the measured and the calculated values of $D_A$ for anions

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<th>% of Clay</th>
<th>Surface area $m^2/g$</th>
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<th>$\tau$ (mes.)</th>
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<th>Ionic strength</th>
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Table 6.8 Effect of temperature on the measured and the calculated values of $D_A$ for cations

| Species | % of Clay | Surface area m$^2$/g | Bulk Density Mg/m$^3$ | $D_A$ (mes.) m$^2$/sec | temp °C | $\mu_{29}/\mu_T$ | Ionic strength | $K_d$ | R | $\Theta_{es}$ | $D_A$ (cal.) {\[\mu=2, mob\]} | $D_A$ (cal.) {\[\mu=9, mob\]} | $D_A$ (cal.) {\[\mu=2, immob\]} | $D_A$ (cal.) {\[\mu=9, immob\]} |
|---------|-----------|----------------------|-----------------------|-----------------------|--------|------------------|----------------|------|----|---------------|----------------|----------------|----------------|----------------|----------------|
| Sr      | 50        | 630                  | 1.73                  | 2.50E-11              | 25     | 1                | 0              | 3    | 5.49 | 0.21          | 3.29E-11         | 1.48E-10        | 6.00E-12        | 2.70E-11        |
|         | 50        | 630                  | 1.72                  | 2.40E-11              | 25     | 1                | 0              | 3    | 5.45 | 0.21          | 3.29E-11         | 1.48E-10        | 6.04E-12        | 2.72E-11        |
|         | 50        | 630                  | 1.73                  | 4.30E-11              | 60     | 1.91             | 0              | 4    | 6.49 | 0.21          | 6.29E-11         | 2.83E-10        | 9.68E-12        | 4.36E-11        |
|         | 50        | 630                  | 1.73                  | 4.10E-11              | 60     | 1.91             | 0              | 4    | 6.49 | 0.21          | 6.29E-11         | 2.83E-10        | 9.68E-12        | 4.36E-11        |
|         | 50        | 630                  | 1.77                  | 6.30E-11              | 90     | 2.82             | 0              | 4.9  | 7.57 | 0.21          | 9.30E-11         | 4.19E-10        | 1.23E-11        | 5.53E-11        |
|         | 50        | 630                  | 1.74                  | 6.30E-11              | 90     | 2.82             | 0              | 4.9  | 7.43 | 0.21          | 9.30E-11         | 4.18E-10        | 1.25E-11        | 5.63E-11        |
|         | 50        | 630                  | 1.62                  | 3.50E-11              | 25     | 1                | 0.27           | 2.6  | 4.68 | 0.21          | 3.25E-11         | 1.46E-10        | 6.94E-12        | 3.12E-11        |
|         | 50        | 630                  | 1.6                   | 6.00E-11              | 60     | 1.91             | 0.27           | 3.6  | 5.62 | 0.2           | 6.18E-11         | 2.78E-10        | 1.10E-11        | 4.95E-11        |
|         | 50        | 630                  | 1.63                  | 6.00E-11              | 60     | 1.91             | 0.27           | 3.6  | 5.72 | 0.21          | 6.21E-11         | 2.80E-10        | 1.09E-11        | 4.89E-11        |
|         | 50        | 630                  | 1.64                  | 1.04E-10              | 90     | 2.82             | 0.27           | 4.6  | 6.75 | 0.21          | 9.20E-11         | 4.14E-10        | 1.36E-11        | 6.13E-11        |
|         | 50        | 630                  | 1.67                  | 9.60E-11              | 90     | 2.82             | 0.27           | 4.6  | 6.86 | 0.21          | 9.24E-11         | 4.16E-10        | 1.35E-11        | 6.07E-11        |
|         | 50        | 630                  | 1.66                  | 4.90E-11              | 25     | 1                | 1.4            | 0.38 | 2.6  | 0.21          | 3.27E-11         | 1.47E-10        | 1.26E-11        | 5.66E-11        |
|         | 50        | 630                  | 1.64                  | 5.20E-11              | 25     | 1                | 1.4            | 0.38 | 2.53 | 0.21          | 3.26E-11         | 1.47E-10        | 1.29E-11        | 5.80E-11        |
|         | 50        | 630                  | 1.65                  | 1.01E-10              | 60     | 1.91             | 1.4            | 0.49 | 2.68 | 0.21          | 6.23E-11         | 2.81E-10        | 2.33E-10        | 1.05E-10        |
|         | 50        | 630                  | 1.65                  | 9.80E-11              | 60     | 1.91             | 1.4            | 0.49 | 2.68 | 0.21          | 6.23E-11         | 2.81E-10        | 2.33E-10        | 1.05E-10        |
|         | 50        | 630                  | 1.67                  | 1.64E-10              | 90     | 2.82             | 1.4            | 0.57 | 2.83 | 0.21          | 9.24E-11         | 4.16E-10        | 3.27E-11        | 1.47E-10        |
|         | 50        | 630                  | 1.69                  | 1.67E-10              | 90     | 2.82             | 1.4            | 0.57 | 2.9  | 0.21          | 9.27E-11         | 4.17E-10        | 3.19E-11        | 1.44E-10        |
6.5 Solution Concentration

To investigate the effect of solution concentration (i.e. ionic strength of the solution) on the diffusion process, other factors suspected to effect this process must be held constant. Therefore, clay density, temperature, type of clay, and the type and the concentration of diffusing species are held constant. The measured $D_A$ values obtained from literature were taken at three elevated temperatures 25, 60, and 90°C for three different ionic strengths of 0, 0.27, and 1.40. These values are presented in Table 6.9 for anions and Table 6.10 for cations. For the given ions and soil, the measured $D_A$ values listed in Table 6.9 and Table 6.10 are found to be linearly related to the ionic strength, i.e. the apparent diffusion coefficient increases as the ionic strength of the solution increases (see Figure 6.18 and Figure 6.19). The variation of the measured values of $D_A$ can be related to two parts: the first part is due to the effect of the ionic strength on the thickness of the double layer. The higher the value of ionic strength, the smaller the thickness of the double layer. The second part is due to the effect of the ionic strength on the distribution coefficient, $K_d$. The distribution coefficient is always determined experimentally when performing diffusion tests for any cation. Oscarson et al. (1984) presented a tabular paper where they listed the measured $K_d$ values for different diffusing species at different environmental conditions (pH level, clay type and temperature). For the given cations, the measured values of $K_d$ are found to be inversely related to the ionic strength of the solution until a certain ionic strength. After this value, $K_d$ is not significantly effected by the increase in the ionic strength. This is illustrated in Figure 6.20 and Figure 6.21. The relation between $K_d$ and ionic strength can be explained by the following: as the ionic
strength of the solution increases, the competition between the diffusing species and the solution cations on the available sites decreases. This reduction will continue until it reaches a time where all available sites are being filled by the solution cations, i.e. no sites are available for the diffusing species.

A comparison between the measured apparent diffusion coefficients obtained from literature and the calculated ones for anions are presented in Table 6.9. The calculated values of $D_A$ are in reasonable agreement with the measured $D_A$. The data listed in Table 6.9 shows that the ionic strength does not have a significant effect on changing the thickness of the double layer. This is because the clay specimen are highly compacted (density $> 1.0 \text{ Mg/m}^3$). At this density the pore space between clay particles are extremely small and the double layer is nearly compressed to its maximum. The calculated values of $D_A$ for cations are varied; this is because some of the variables should have been experimentally determined and they were not available at the time of the study. Hence, these variables were assumed within a reasonable range. The data presented in Table 6.10 shows that the adsorption coefficient $K_d$ values are significantly effected by the ionic strength of the solution.

Concluding this section, the distribution coefficient, $K_d$, values are significantly effected by the ionic strength of the solution, while the thickness of the double layer are not. Hence the effect of ionic strength on the double layer can be neglected for compacted clay.
Figure 6.18 Effect of ionic strength on the apparent diffusion coefficient for Chlorine

Figure 6.19 Effect of ionic strength on the apparent diffusion coefficient for Strontium
Figure 6.20 Effect of ionic strength on adsorption coefficient for Americium (Oscarson et al. 1984)

Figure 6.21 Effect of ionic strength on adsorption coefficient for Strontium (Oscarson et al. 1984)
Table 6.9 Effect of solution concentration on the measured and the calculated values of $D_\lambda$ for anions

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<th>$D_\lambda$ (mes) m$^2$/sec</th>
<th>Ionic strength</th>
<th>Clay Density Mg/m$^3$</th>
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6.6 Summary

A parametric analysis for some selected parameters was discussed and thoroughly examined. The analysis showed that the viscosity of the pore solution and the distribution coefficient are affected by temperature and ionic strength respectively. It also showed that the porosity of dead-end pores is an important parameter to be included in predicting the diffusion coefficient. Based on the above results, the apparent diffusion coefficient at steady-state, $D'_A$, and at transient-state, $D_A$, can be simplified as follows:

$$D_A = D_p = D_o \tau \mu_i$$

$$D'_A = D_p \theta = D_o \tau \mu_i \delta_i \theta i_g$$

where $i$ represents the diffusive pathway (surface or interstitial water). The term $i_g$ is the gradient factor and it is expressed as follows:

$$i_g = \frac{K_d \gamma_d}{\theta} m_i$$

where $m_i$ is the mobility factor and it is expressed as the percentage of mobile species. For non-sorbed species and totally immobile species $i_g$ is equal to 1, whereas, for totally mobile species $i_g$ is equal to $K_d \gamma_d / \theta$ and for partially sorbed mobile species $i_g$ falls between 1 and $K_d \gamma_d / \theta$. Replacing $\tau$ and $\delta_i \theta$ by $\theta_n$, the diffusion coefficient can be written as:

$$D_A = D_p = D_o \theta c_i \mu_i$$

and

$$D'_A = D_p \theta = D_o \theta c_i^2 \mu_i i_g$$

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CHAPTER 7

Conclusions and Recommendations

7.1 Conclusions

The following conclusions can be drawn from this study are:

1) The diffusion mechanism is thoroughly investigated and the parameters affecting the diffusion coefficient are identified and evaluated.

2) A clay-water-interaction model has been developed which allow the diffusion coefficient of contaminants as a function of clay minerals, clay density, and environmental factors to be predicted using simple parameters.

3) The clay-water-interaction model can be applied to a clay-sand mixture as the diffusion coefficient is shown to be controlled mainly by the clay content.

4) The tortuosity factor can be better approximated by the effective porosity than the total porosity used in the past. A relationship between the tortuosity factor and effective porosity has been established.
5) The methodologies commonly used to determine the apparent diffusion coefficients are assessed. The diffusion coefficients from these methods are interpreted to address the discrepancies of data existing in literature.

7.2 Recommendations

Further work is recommended in the following areas:

1) To identify the factors (such as clay type, clay density, pore water salinity, and temperature) affecting the distribution coefficient.

2) To investigated the mobility of the adsorbed species. This work is required for further development of the clay-water-interaction model.

3) To further investigate the clay-water-interaction model for loose clay with various water salinities.
References


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APPENDIX A

Table A.1 Physical properties of water\textsuperscript{13}

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\textsuperscript{13} Data from Robinson and Stokes 1959

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APPENDIX B

B.1 Calculation of the Porosity Terms

a) Total porosity $\theta$ :

$$\theta = 1 - \frac{\gamma_d}{G_s}$$

where $\theta$ = total porosity.

$\gamma_d$ = clay density.

$G_s$ = specific gravity

b) Surface porosity $\theta_s$ :

$$w = \frac{H \times SA}{10000}$$

$$\theta_s = w \times \gamma_d$$

where $w$ = water content.

$H$ = thickness of the diffuse double layer.

$SA$ = specific surface area.
c) Free or interstitial porosity $\theta_i$

$$\theta_i = \theta - \theta_s$$

EXAMPLE \(^{15}\)

\[ g_d = 0.92 \text{ Mg/m}^3 \]
\[ S\text{A} = 480 \text{ m}^3/\text{g} \]
\[ G_s = 2.65 \]
\[ H = 5 \text{ Å} \]

\[
\theta = 1 - \left( \frac{0.92}{2.65} \right) = 0.653
\]

\[
w = 5 \times 480 / 10000 = 0.24
\]

\[
\theta_s = 0.24 \times 0.92 = 0.221
\]

\[
\theta_i = 0.653 - 0.221 = 0.432
\]

\(^{15}\) The values are taken from table 6.1.

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B.2 Calculation of the Clay Density

\[
\text{Weight of sand} = \text{sand content}\% \times \gamma_b
\]
\[
\text{Weight of clay} = \text{clay content}\% \times \gamma_b
\]
\[
\text{Volume of sand} = \frac{\text{weight of sand}}{G_s}
\]
\[
\text{Volume of clay} = 1 - \text{volume of sand}
\]
\[
\text{Clay density} = \frac{\text{weight of clay}}{\text{volume of clay}}
\]

\textit{EXAMPLE}\(^{16}\)

\[
\gamma_b = 1.25 \text{ Mg/m}^3
\]
\[
\text{clay content} = 25\%
\]
\[
G_s = 2.65
\]
\[
\text{weight of sand} = 0.75 \times 1.25 = 0.9375 \text{ g}
\]
\[
\text{weight of clay} = 0.25 \times 1.25 = 0.3125 \text{ g}
\]
\[
\text{volume of sand} = \frac{0.9375}{2.65} = 0.354 \text{ cc}
\]
\[
\text{volume of clay} = 1 - 0.354 = 0.646 \text{ cc}
\]
\[
\text{Clay Density} = \frac{0.3125}{0.646} = 0.48 \text{ Mg/m}^3
\]

\(^{16}\) The values are taken from table 6.4

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APPENDIX C

Clay Mineralogy

Clay liners are composed of cohesive soil, engineered and compacted to prevent contaminant migration, i.e. to act as a sealant. From an engineering point of view the term clay can be defined in several ways, but from a geotechnical and environmental point of view there are two main definitions: (1) clay soil, which refers to all soil particles that have a size of less than 0.002 mm (Mitchell 1976) and (2) clay mineral, which refers to soils that contain an appreciable amount of clay minerals and has plasticity and cohesive. Clay minerals are usually formed from the chemical weathering of certain rocks; they are hydrous alumino silicates. In this study the term clay mineral is used to describe the soil used.

It is known that the characteristics of fine grained materials such as grain size, distribution and grain shape has significant effects on the engineering behavior of the soil, whereas the presence of water does not. On the other hand, the presence of water has significant effects on the engineering behavior of clay minerals. Moreover, the presence of small amounts of clay minerals in a soil mass can markedly effect the behavior of that mass. This influence can be illustrated by the addition of bentonite to a fine grain soil; bentonite is a clay mineral which is mainly composed of sodium montmorillonite. An
addition of 2 to 3 weight percent of bentonite can reduce the soil permeability by 2 to 3 percent and thus reduce the contaminant migration. The influence of clay minerals on a soil's behavior increases by increasing the clay content to a range of 33 to 50 percent, at which point the nonclay particles are essentially floating in a clay matrix and has little effect on the engineering behavior of the soil (Mitchell 1976, Holtz and Kovacs 1981).

It is useful to have a general understanding of the clay that is used as a sealant in most of the recently designed landfill disposal sites. This chapter briefly describes the structure of important clay minerals which is fundamentally important for a good understanding of how they interact with water and each other. For a more thorough understanding of clay mineralogy, the reader is refereed to Grim 1962, and Mitchell 1976.

C.1 Clay Mineral Structure

The structure of clay minerals consists of stacking of two fundamental crystal sheets, the tetrahedral or silica sheet and the octahedral or aluminum sheet. The particular way in which these sheets are stacked together with different binding and different metallic ions in the crystal results in different types of clay minerals.

The tetrahedral sheet consist of a silicon atom, Si, surrounded by four oxygen atoms, O, equidistance from the silicon, as shown in Figure C.1(a). The oxygen are arranged in tetrahedral coordinates and the ones at the base are shared by two silicones of adjacent sheets, see Figure C.1(b). Since silicon has a positive valance of 4 and oxygen has
a negative valance of 2, this sharing will result in a negative charge of 1 on the tetrahedral sheet. If the top oxygen reacts with hydrogen having a positive charge of 1, the sheet will be neutral. Figure C.1(d) shows how these sheets are joined together to form a hexagonal network with a hexagonal hole, it also shows that the oxygens at the base of the sheet are in one plane and the tip ones all pointed in the same direction. A common schematic used to represent the tetrahedral sheet is shown in Figure C 1(c).

The octahedral sheet consists of an aluminum or magnesium atom surrounded by six oxygen or hydroxyl atoms. The oxygens and the hydroxyls are arranged in octahedral coordinates and they are equidistance from the aluminum or the magnesium atom, as shown in Figure C 2(a). Figure C 2(b) shows that each of the oxygens and hydroxyls are shared by the neighboring octahedral to form a sheet structure. A common schematic used to represent the octahedral sheet is shown in Figure C 2(c). The substitution of different cations in the octahedral sheet is common and leads to different clay minerals. Since this substitution does not change the crystal structure, it is called isomorphous substitution. If all oxygens are replaced by hydroxyls and aluminum is the cation, then only two-third of the possible positions are filled to balance the structure and the resulting mineral is called Gibbsite. If magnesium is substituted for the aluminum, then all the octahedral positions are filled and the mineral is called Brucite.

---

17 Isomorphous substitution: is the substitution of similar size cation with similar or different valence for those presented in the ideal crystal structure without causing changes in the structure. Common cation substitution in clay minerals includes aluminum (Al\(^{3+}\)) for silicon (Si\(^{4+}\)), magnesium (Mg\(^{2+}\)) for aluminum (Al\(^{3+}\)), and ferrous (Fe\(^{2+}\)) for magnesium (Mg\(^{2+}\)). Isomorphous substitution in clay minerals results in a charge deficiency in the crystal structure and a net negative charge on the mineral's surface.
Figure 2.1  (a) Single silica unit layer  (b) Silica sheet  (c) Schematic representation of the silica sheet  (d) Top view of the silica sheet
Figure 2.2 (a) Single aluminum layer  (b) Aluminum sheet  (c) Schematic representation of the aluminum sheet  (d) Top view of the aluminum sheet
Clay minerals can be roughly categorized into four main groups based on the height of the unit cell, the composition of the sheets and the kind of intersheet bonding that forms the layers of unit cells. These groups are: kaolinite, illite, chlorite and smectite. The following sections briefly describes these groups discussing the engineering behavior of one sample of each group.

C.1.1 Kaolinite Group

Kaolinite is the most common mineral in this group. The basic structure of this mineral is composed of stacks of 1:1 unit cells. Each unit cell consists of a sheet of silica tetrahedral and a sheet of aluminum octahedral. The two sheets are held together in such a way that the tips of the tetrahedral all point toward the center of the unit cell where they share the oxygen atom to form a single plane. The remaining atoms in the plain are hydroxyls (OH) and are located so that each atom is directly below the hexagonal hole in the silica network, as shown in Figure C.3. Successive layers of the basic structure are held together by Van der Waals force and by hydrogen bonds between the hydroxyls of the octahedral sheet and the oxygen of the tetrahedral sheet. Since the hydrogen bond is very strong, it prevents hydration (penetration of water between successive layers) and allows the layers to stack up to make a rather large crystal. A typical kaolinite crystal can be 70 to 100 layers thick (Mitchell 1976, Young 1966, Grim 1962, Holtz and Kovacs 1981). The height of the kaolinite unit cell is 7.2 Å and the specific surface area is on the order of 10 to 20 m²/g of dry clay.
A small net negative charge exists on the surface of kaolinite minerals. This charge results from the small amount of isomorphous substitution that takes place in the silica or the gibbsite sheet and has the ability to exchange cations with a capacity of 3 to 15 meq/100g.

Kaolinite is usually stacked in a blocky form and usually exists in larger size and lower surface to volume ratio compared to other clay minerals. This lower surface area, combined with the relatively small negative surface charge, results in kaolinite being the least electrochemically active and the least plastic clay mineral.

Compared with other clay minerals, kaolinite has a lower affinity for water, lower dispersivity, and does not achieve low permeability upon compaction. On the other hand, because it is not electrochemically active, its behavior may be less affected by chemicals than other clay minerals. Thus, kaolinite minerals may have a higher permeability than other clay minerals, but its permeability may not be as sensitive to change in moisture content or to chemicals attack compared to other clays (Goldman 1990).

**C.1.2 Illite Group**

Illite minerals are also known as mica-like clay minerals because their basic structural unit is similar to that of hydrous mica. Illite is the common mineral in this group and it is composed of a stack of 2:1 unit cells. The basic unit structure of illite consists of a sheet of aluminum octahedral sandwiched between two sheets of silica tetrahedral. As
shown in Figure C.4 the sheets are arranged so that the tips of the tetrahedral sheet all pointed toward the center and the oxygen forming the tips of the tetrahedral are shared with the octahedral sheet. Illite layers are bonded together with a potassium atom resulted from the isomorphous substitution of aluminum for silicon in the tetrahedral sheet (to balance the negative charge). The potassium atom fits tightly in the hexagonal hole in the silica sheet (see Figure C.4) and it is not exchangeable. As a result, a strong bond exists between the layers. The height of the illite layer ranges from 10Å to 14Å.

Compared with other clay minerals, illite has an intermediate surface to volume ratio (65 to 100 m²/g), a medium cation exchange capacity (10 to 40 meq/100g) and a medium reaction to chemicals. Because of the strength of the interlayer potassium bond, it effectively prevents hydration and intercalation of organic liquids and other cations (Holtz and Kovacs 1981, Goldman 1990).

C.1.3 Chlorite Group

Chlorite mineral usually exists in nature combined with other minerals. The structure of this mineral is composed of a stack of 2:1:1 unit cells. Each unit cell consists of a gibbsite or a brucite sheet sandwiched between two silica tetrahedral sheets, with another brucite sheet sandwiched between the two layers, as shown in Figure C.5. The height of the unit cell is 1.4 nm.
Figure C.3 Kaolinite structure

Figure C.4 Illite structure
Compared with other clay minerals, chlorite is less active than smectite, their cation exchange capacity ranges from 10 to 40 meq/100g and their engineering behavior may be similar to the illite minerals. Isomorphous substitution do exist and this results in a net negative charge on the surface of the chlorite mineral. Therefore, water will be adsorbed between the layers to balance the negative charge.

C.1.4 Smectite Group

The smectite may be divided into two groups, based on the composition of the octahedral sheet: the montmorillonite, which has a dioctahedral (gibbsite sheet), and the saponites, which has a trioctahedral (brucite sheet). In this study only the montmorillonite will be looked at.

Montmorillonite

The basic structure of the montmorillonite minerals is composed of a stack of 2:1 unit cells. Each unit cell consists of a dioctahedral sheet (gibbsite) sandwiched between two silica tetrahedral sheets. These sheets are arranged so that all the tips of the tetrahedral point toward the center of the unit cell. The oxygen atoms forming the tips of the tetrahedral are shared with the octahedral sheet and the remaining atoms are hydroxyls. These hydroxyls are arranged so that they are directly above and below the hexagonal hole formed by the silica tetrahedral sheets. Figure C.6 illustrate the basic structure of montmorillonite.
Extensive isomorphous substitution often occurs in the montmorillonite minerals, such as the substitution of magnesium and other cations (called exchangeable cations, like Fe, Cr, Zn, Li) for aluminum and sometimes aluminum for silicon (Mitchell 1976). The substitution of higher positive valance for that of lower valance results in charge a deficiency, in other words, a net negative charge will result on the surface of the montmorillonite minerals. This charge deficiency is usually balanced by exchangeable cations that are positioned between the layers and on the surface of particles. These minerals exhibit high cation exchange capacity (usually around 80 to 150 meq/100g, Mitchell 1976) due to the large amount of substitution that occurs.

In montmorillonite stacking, the oxygen plane of each layer is adjacent to another oxygen plane of a neighboring layer. This arrangement results in a weak bonding between the layers; therefore, water molecules and polar fluids can easily penetrate the unit layers. The penetrated water is adsorbed on the oxygen plane by establishing hydrogen bonds; since this is a strong bond, water can not be easily separated from the montmorillonite mineral. As a result, montmorillonite particles are very small and can be dispersed to sheets of unit layer thickness of 10Å in water. This dispersion results in a very high specific surface area with a primary surface area of 50 to 120 m²/g and a secondary surface area of 700 to 840 m²/g (Goldman 1990).

The type of the exchangeable cations strongly influences the behavior of montmorillonite. The most commonly occurring cations are calcium and sodium. When
Figure C.5 Chlorite structure

Figure C.6 Montmorillonite structure
calcium is the exchangeable cation, the amount of interlayer water is limited and the maximum height of the unit layer of calcium montmorillonite is 19Å (Goldman 1991). However, if sodium is the exchangeable cation, the amount of interlayer water is not limited and the height of the unit layer of sodium montmorillonite can range from 10Å to complete separation. This results in high swelling, which is the main characteristic of sodium montmorillonite.

Compared with other clay minerals, montmorillonite has weak bonds between its unit layers a very high specific surface area and a large degree of swelling. The large degree of swelling is due to the hydration of the interlayer cations and also because the large hydration energy involved is able to overcome the attractive forces between the layers. Because of the high specific surface area, montmorillonite is the most active clay mineral to chemical attack (i.e. react with chemicals).

Bentonite

Bentonite is not a clay mineral. It is a commercial name for rocks or clay deposits composed largely of the clay mineral montmorillonite. The swelling and dispersive properties of this mineral gives bentonite the ability to lower the permeability of a soil, even when added in a small quantities. The swelling capacity of bentonite depends on its sodium-montmorillonite content. Low-swelling bentonite has significant quantities of calcium-montmorillonite, which, because of limited interlayer water uptake, does not swell to the extent of sodium-montmorillonite. High-swelling sodium bentonite has a liquid limit
of 500 percent or more and can swell 15 to 20 times in volume (Grim 1962). Calcium bentonite will increase in volume from 0 to 5 times when wetted with water, this swelling capacity has been reported to increase 700 to 1000 percent by treating calcium bentonite with a 0.25 percent solution of \( \text{Na}_2\text{CO}_3 \) (Goldman 1990).

**C.2 Clay water interaction**

It has been mentioned previously that the presence of water does not have much effect on the engineering behavior of fine grain soil. Whereas, the presence of water in clay minerals, specially montmorillonite, have a significant effect on their engineering behavior. The importance of water in clay arises from the net negative charge that exists on clay surface and from the large specific surface area which clay has. The previous section showed that as the size of clay particles reduces the specific surface area increases, thus the activity of the particle will increase, i.e. the surface will be more active\(^\text{18}\).

The negative charges are unevenly distributed on the surface of the clay particle, while the edges have positive and negative charges. As a result of this charge distribution clay particles repel each other, unless edge-to-surface contact. Because of the large net negative charge, clay particles attract cations, such as potassium, sodium, calcium, to obtain an electrically balanced or equilibrium condition.

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\(^{18}\) The activity of clay can be defined as: \( A = \text{PI/clay fraction} \), where the clay fraction is usually taken as the particles less than 2 \( \mu \text{m} \). Therefore, the smaller the particle, the more active its surface will be.
Cations are positively charged particles; in turn they attract negatively charged particles to their surface. As a result of this, water molecules will be attracted to these particles. A water molecule is known to be neutral by itself, but its oxygen and hydrogen atoms are arranged in such a manner that the center of gravity of the positive and negative charges do not coincide. The resulting molecule has a plus charge acting on one end and a negative charge acting on the other end. Thus, a water molecule can be considered as a polar molecule, see Figure C.7. The negatively charged end of the water molecule is attracted to the cation, which in turn is held by the clay particle. Other water molecules may directly attracted to the surface of the clay particles. The resulting effect is that a significant amount of water will become bonded to the surface of the clay particle, see Figure C.8.

As a result of the above, clay particles are always hydrated, i.e. surrounded by layers of water called adsorbed water. Since the movement of contaminants or any species through these minerals are strongly influenced by the adsorbed water layers, these water layers should be considered part of the clay mineral when studying the migration process. Along with that, the engineering behavior of clay minerals will change as the thickness of this hydration shell increases. The attraction force between clay and water arises from both: the negative charge that exists on the surface of the clay particles, and from the structure of the water molecule. As a result of this attraction, hydrogen bonds between clay and water ions will develop. Since hydrogen bonds are extremely strong, adsorbed water can not be easily separated from the surface of clay particles. Cations in water are
always hydrated and they are exchangeable. Therefore, the exchangeable cations held near the negatively charged surface hooked in some of the water at the surface as water of hydration of ions. Since species are hydrated to different degrees, the hydration of the clay surface would vary depending upon the species present.

It is incorrect to picture adsorbed water as a dipole molecules lined up uniformly at the surface with positive ends on the clay and negative ends away from it. The surface density of negative charges on the clay is too small to let water molecules to arrange in this way. The first layer of water is held by hydrogen bonding to the clay surface and the second layer of water is held again by hydrogen bonding to the first layer but the bonding force become weaker. Each successive layer is held less strongly and the bonding quickly decreases to that of free water. The properties of the water layer close to the clay surface differ from those of free water. For example, the density of adsorbed water is higher than that of free water. Some studies showed that values of up to 1.4 g/cc have been measured for the first layer. The density is found to decrease away from the surface of clay particles, dropping to 0.97 g/cc at about the fourth water layer, and then increases to 1 g/cc for free water. This difference in water density will strongly effect the migration of contaminant in these layers, as the density of water increases the migration process decreases.

From the above it is clear that the viscosity of water decreases away from the surface of clay particles and it will continue until it become free water. The rate of this decrease requires further studies, therefore. two types of water has been considered in this study: surface water and free water.
Figure C.7  (a) Model of water molecule (b) relative location of atoms in the water molecule (c) polar representation of water molecule

Figure C.8  Adsorbed water and cations in diffuse double layer surrounding clay particle