# Diffusive characteristics of contaminants in clayey soil and hardened barrier materials

## Les caractéristiques diffusives des contaminants dans les sols argileux et les matériaux isolants durcis

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ABSTRACT: Diffusive characteristics of inorganic chemicals, i.e. NaCl, KCl and $CaCl_2$, in clayey soils and hardened barrier materials located under a seashore waste landfill near Seoul, Korea, are analyzed through laboratory column test and compared with those published in various literatures. The soil samples were sectioned after the experiment was finished and the concentrations of the chemicals were measured. Diffusion coefficients and retardation factors were determined by using one-dimensional solute transport numerical program. The diffusion coefficients ($D^*$) obtained for chloride in clayey soils were in between $2.5 \times 10^{-10}$ $m^2/s$ and $5.5 \times 10^{-10}$ $m^2/s$. The average diffusion coefficients ($D^*$) for chloride diffusion in silicate dominated layer (PA) and calcium dominated layer (PB) are $1.9 \times 10^{-10} m^2/s$ and $1.65 \times 10^{-10} m^2/s$, respectively. These values were about 50–60% lower than those in clayey soils. The $D^*$ values of clayey soils are lower than those of clayey till which has relatively large fraction of coarse grains.

RÉSUMÉ: Les caractéritiques diffusives des produits chimiques inorganiques, à savoir NaCl, KCl et $CaCl_2$, dans les sols argileux et les matériaux isolants durcis situés sous un terrain comblé de déchets au bord de la mer près de Séoul, Corée du Sud, sont analysées dans la laboratoire par le test de colonne et comparées avec celles qui sont publiées dans les divers documents. Les échantillons de terre sont sectionnés à la fin de l'expérimentation et les concentrations des produits chimiques sont mesurées. Les coéfficients de diffusion et les facteurs de retardement sont déterminés en utilisant la programmation numériques de transport unidimmenionnel de soluté. Les coéfficients de diffusion($D^*$) obtenus pour le chlorure dans les sols argileux ontété entre $2.5 \times 10^{-10} m^2/s$ et $5.5 \times 10^{-10} m^2/s$ Les coéfficients de diffusion($D^*$) moyens pour la diffusion de chlorure dans la couche dominée par silicate(PA) et la couche dominée par calcium(PB) sont respectivement $1.9 \times 10^{-10} m^2/s$ et $1.65 \times 10^{-10} m^2/s$ Cettes valeurs sont à peu près de 50 à 60% plus basses que celles dans les sols argileux. La valeur $D^*$ des sols argileux sont plus basse que celles de sol glaciaire qui a relativement une grande fraction de gros grains.

## 1 INTRODUCTION

After 1990s, it becomes an important issue to prevent the contamination of the soil and groundwater in Korea, since rapid industrialization and high population in municipals cause the environmental pollution. In order to find the contamination of soil and groundwater, it is necessary to evaluate the mechanism of migration of contaminants through soil and groundwater and the ability of reducing contaminant of barrier materials. For situations where the clayey barrier has very low hydraulic conductivity with low hydraulic gradient, contaminant transport will be very slow and is controlled by diffusion through the clay pore fluid (Barone et al. 1989). The studies of diffusion-dominant transport and sorption through clayey soils are required because the information of diffusive transport through domestic fine-grained materials is not sufficient.

In this paper, pure diffusion tests are performed in order to analyze diffusive characteristics of inorganic chemicals, i.e. NaCl, KCl and $CaCl_2$, in clayey soils and hardened barrier materials, i.e. silicate dominated soil (PA) and calcium dominated soil (PB) mixed with clayey soils located under the seashore waste landfill. Diffusion coefficients and retardation factors were determined by using one-dimensional solute transport numerical program and compared with those published in various literatures.

## 2 THEORETICAL BACKGROUND

Diffusion is a main transport characteristic for fine-grained materials, e.g. landfill liners used to prevent the migration of contaminants from waste landfills. The equation describing advection-dispersion transport of a reactive solute in a saturated porous medium can be written in one-dimensional form as (Freeze & Cherry, 1979):

$$\frac{D}{R}\frac{\partial^2 c}{\partial x^2} - \frac{\bar{v}}{R}\frac{\partial c}{\partial x} = \frac{\partial c}{\partial t} \qquad (1)$$

where $c$ is the concentration of solute in the solution phase $[M/L^3]$; $t$ is time [T]; $D$ is the dispersion coefficient of the solute in the porous medium $[L^2/T]$; and $R$ is the retardation factor Retardation factor is given as:

$$R = 1 + \rho K_d / n \qquad (2)$$

where $\rho$ is the bulk density of the porous medium $[M/L^3]$; $K_d$ is the distribution coefficient $[L^3/M]$ and $n$ is porosity. The dispersion coefficient, $D$, can be defined by

$$D = \alpha \bar{v} + D^* \qquad (3)$$

where $\alpha$ is the dispersivity and $D^*$ is the effective diffusion coefficient of solute in the porous medium $[L^2/T]$. Diffusion coefficients, and retardation factors, $R$, are obtained by using the transport program CDFD (convection-dispersion finite difference).

In the computer program CDFD, an analytical solution (Bear 1972) is also stored to verify the numerical solution of the one-dimensional dispersion-convection equation (1). The analytical solution is in the form :

$$\frac{C}{C_o} = \frac{1}{2}\left[ erfc\left(\frac{l - \bar{v}_l t}{2\sqrt{D_l t}}\right) + \exp\left(\frac{\bar{v}_l l}{D_l}\right) erfc\left(\frac{l + \bar{v}_l t}{2\sqrt{D_l t}}\right)\right] \qquad (4)$$

where $C_0$ is initial concentration and *erfc* is complementary error function and the initial and boundary conditions for this formula are :

Table 1. Physical properties of soils (Sudokwon 1995).

| $G_s$ | $w$ (%) | LL (%) | PL (%) | PI (%) | $\gamma_{sat}$ (t/m³) | $\gamma_{dmax}$ (t/m³) | $w_{opt}$ (%) | Grain size (%) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Silt | Clay | Sand |
| 2.68 | 35 | 42 | 25.46 | 16.54 | 2.02 | 1.78 | 13.5 | 63 | 25 | 12 |

Table 2. Chemical components in the hardened barrier (Sung-Jung 1998).

| Components | | $K_2O$ | CaO | $SiO_2$ | MgO | $Na_2O$ | $Al_2O_3$ | $Fe_2O_3$ | $SO_3$ | Organic content | Others |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Per-centage (%) | PA | 1.10 | 12.30 | 62.00 | 3.54 | 13.20 | 2.82 | 0.58 | 3.66 | 0.30 | 0.50 |
| | PB | 0.48 | 84.60 | 4.27 | 2.48 | 0.40 | 1.53 | 0.47 | 0.30 | 4.93 | 0.54 |

$$C(l,0)=0 \qquad l \geq 0 \tag{5a}$$

$$C(0,t)=C_o \qquad t \geq 0 \tag{5b}$$

$$C(\infty,t)=0 \qquad t \geq 0 \tag{5c}$$

The relation of diffusion coefficient and retardation factor can be expressed by:

$$D_{Na}=\frac{D_{Cl}}{R_{Na}},\quad D_K=\frac{D_{Cl}}{R_K},\quad D_{Ca}=\frac{D_{Cl}}{R_{Ca}} \tag{6}$$

where $D_{Cl}$ is the diffusion coefficient of non-reactive solute, $Cl^-$, and $D_{Na}$, $D_K$ and $D_{Ca}$ are the diffusion coefficients of reactive solutes, $Na^+$, $K^+$ and $Ca^{2+}$, respectively.

## 3 MATERIALS AND METHOD

### 3.1 *Materials*

The seashore clayey soil used in the study is obtained from Sudokwon Metropolitan landfill and the properties of the soils are presented in Table 1.

The chemical components of the hardened barrier materials were identified based on KS 15129 in Table 2. Fraction of CaO in PB in upper barrier of the Sudokwon Landfill is 84.6% and fraction of $SiO_2$ in PA in lower barrier is 62% (Sung-Jung Industry, 1998).

These materials are constructed by mixing with the in-situ clayey soil and compacted to 95% of $\gamma_{dmax}$ = 1.754t/m³. Mixing ratio of the hardened barrier samples is shown in Table 3.

The chemical properties of leachate and porewater obtained in Sudokwon Landfill are summarized in Table 4. The high concentration of chloride ion is attributed to salt water in seashore clayey soils. Porewater is the surface water samples in the landfill mixed with rainwater.

Background concentration of the inorganic chemicals used in the experiment is determined from the chemical properties of porewater in Table 4. Soil samples in the test columns are saturated with porewater. For solute which represents the leachate in the landfill, chloride ($Cl^-$) is selected as a principal tracer. Sodium ($Na^-$), potassium ($K^+$) and calcium ($Ca^{2+}$) are chosen as primary reactive elements. Solutes of three inorganic chemicals, i.e. NaCl, KCl and $CaCl_2$, are produced based on the concentration of chloride, 12,000mg/l, which is the approximated concentration of chloride in the leachate (Table 4).

### 3.2 *Experimental Setting*

The columns of diffusion experiment are designed to simulate simple, one-dimensional contaminant migration through seashore clay liner and hardened barrier materials (Fig. 1). Each column consists of a hollow cylinder with the thickness 10mm, the interior diameter 10cm and the height 15cm. A porous plate of thickness 8mm is placed at the top of the soil surface and under the bottom of column. A sampling port is located at top plate and a drainage outlet at the column base.

The test specimens of clayey soil are prepared by mixing air-dried soil with porewater until the desired moisture content is obtained. Then the mixed soils are compacted into molds. The soil samples and hardened barrier materials are soaked with pore water prior to diffusion tests. Simulated leachates of single components, i.e. NaCl, KCl and $CaCl_2$, are introduced into the top of column and the temperature of the laboratory is kept in the range of 21℃ and 25℃. Leachate in the reservoir was stirred and monitored periodically by withdrawing water samples through the sampling port (Fig. 1). Concentrations of cations adjusted to chloride concentration, 12,000mg/L are given in Table 5.

Table 3. Mixing ratio of the hardened barrier samples.

| Sample | | Weight (g) | | | Mixing ratio |
|---|---|---|---|---|---|
| Hardened barrier materials | PA mixed with clayey soil | PA | Clayey soil | Water | PA : clayey soil = 1: 5 |
| | | 229.1 | 1145.4 | 185.54 | |
| | PB mixed with clayey soil | PB | Clayey soil | Water | PB : clayey soil = 1: 6.67 |
| | | 179.2 | 1195.2 | 185.54 | |

Table 4. Chemical properties of leachate and porewater (Song 1999).

| Type | Atomic weight | Leachate | | Porewater | |
|---|---|---|---|---|---|
| | | mg/L | meq/L | mg/L | meq/L |
| $Cl^-$ | 35.5 | 12,000 | 332.4 | 5500 | 154.9 |
| $Na^+$ | 22.9 | 2400 | 104.8 | 1452 | 63.4 |
| $K^+$ | 39.1 | 1430 | 36.6 | 79.5 | 2.0 |
| $Ca^{2+}$ | 24.3 | 107.4 | 2.7 | 1800 | 74.1 |

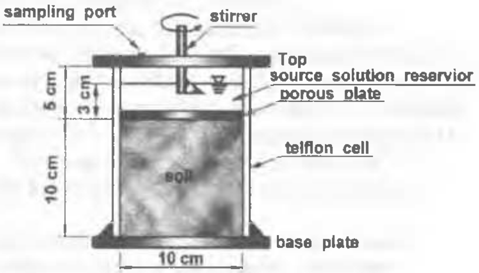

Figure 1. Schematic diagram of the diffusion apparatus.

When the diffusion tests are completed, the soil samples in the diffusion cell are extruded and sectioned into 8mm thick slices. These slices are used to obtain the vertical distribution of the concentration of the selected chemicals. Chloride ion concentrations in pore water are determined by specific ion electrode (model 290A, Orion) and concentrations of sodium, potassium and calcium are measured using a flame atomic absorption spectrometer (model AA-6800, SHIMADZU) with auto sampler and readjust lamp. The pore water samples squeezed from the sliced soil are diluted to bring the concentrations into the measurement range of the instrument.

## 4 RESULTS

### 4.1 *Clayey soils*

The relative concentrations of solutes in the pore water of the soil versus depth are given in Figure 2 & 3 with the curve of numerical fitting. Values of effective diffusion, D*, were determined by varying D* until the normalized concentration profile is predicted by the computer program CDFD. In these profiles, the concentration of solutes in the source chamber is given by a constant $C_0$ and the background concentration by a constant $C_I$.

To estimate the accuracy of numerical solution, the concentration profile of analytical solution (Bear 1972) for NaCl profile in the soil was fit to the concentration profile from the numerical solution (Fig. 2). The concentration profiles obtained both from the analytical and the numerical analysis are well agreed.

In Figure 3, an average concentration profile from numerical analysis is fit to all concentration profiles obtained from laboratory diffusion tests for $Cl^-$. D* of $Cl^-$ obtained from the fitting is

Table 5. Concentration of inorganic chemicals for diffusion test (Song 1999).

| Chemicals | Initial concentration (mg/L) | | Background concentration (mg/L) | |
|---|---|---|---|---|
| | Cation | Anion | Cation | Anion |
| NaCl | 7795 | 12,000 | 1452 | 6000 |
| KCl | 13,220 | | 80 | |
| $CaCl_2$ | 6783 | | 1200 | |

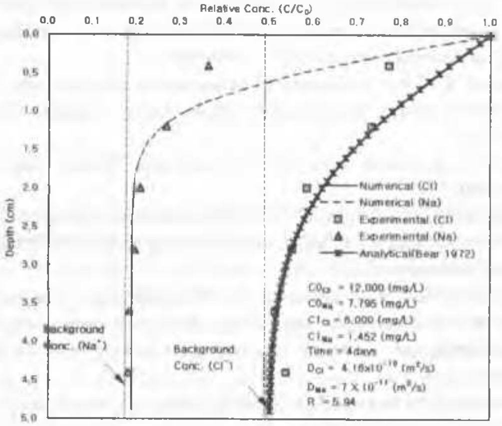

Figure 2. Relative concentration versus depth for diffusion of NaCl through clayey soil.

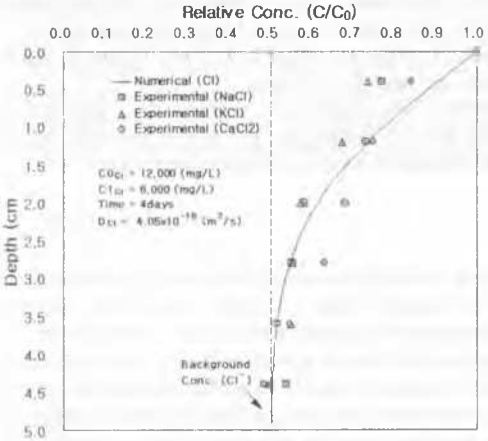

Figure 3. Relative concentration versus depth for diffusion of $Cl^-$ through clayey soil.

$4.05 \times 10^{-10} m^2/s$. The variations of concentration distribution for three inorganic chemicals in Figure 3 seems to be caused by various reasons, e.g. the minor heterogeneity of remolded soil samples, error of concentration measurement, and the interaction between $Cl^-$ and cations, i.e. $Na^+$, $K^+$ and $Ca^{2+}$. The effective diffusion coefficients for chloride ion varied from $2.5 \times 10^{-10} m^2/s$ to $5.5 \times 10^{-10} m^2/s$, and the $D^*$ values for cations of sodium, potassium and calcium are in the range of $0.7 \times 10^{-10} m^2/s$ and $1.5 \times 10^{-10} m^2/s$, owing to the adsorption effect.

### 4.2 *Hardened Barrier Materials*

The concentration profiles of $Cl^-$ for PA, PB mixed soil is obtained by the laboratory diffusion test and fitted to the data from the numerical analysis in Figure 4 and 5. The concentration profiles of the chloride are quite similar among the three solutes tested and the effective diffusion coefficients obtained from the numerical analysis are $1.9 \times 10^{-10} m^2/s$ for PA and $1.65 \times 10^{-10} m^2/s$ for PB.

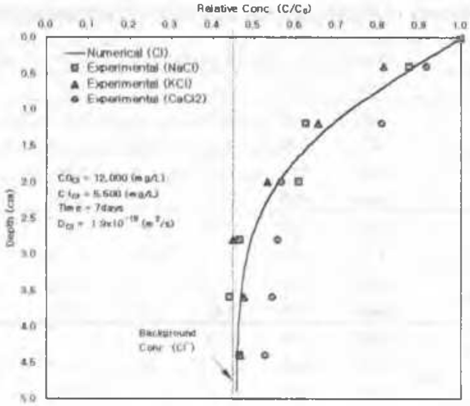

Figure 4. Relative concentration versus depth for diffusion of $Cl^-$ through PA mixed with soil.

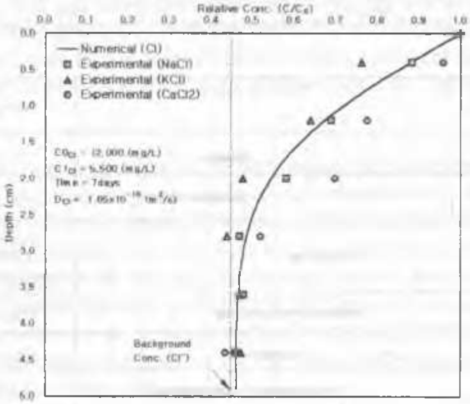

Figure 5. Relative concentration versus depth for diffusion of $Cl^-$ through PB mixed with soil.

## 5 DISCUSSION

The diffusion coefficients, $D^*$, of chloride obtained from the laboratory column test are summarized in Table 6. The average effective diffusion coefficients of PA, PB mixed soil $1.9 \times 10^{-10} m^2/s$, $1.65 \times 10^{-10} m^2/s$, respectively. These values are 50% lower than those of clayey soil. This reduction seems to be caused by the increase of the density of the hardened barrier materials due to compaction and curing.

The retardation factors for reactive solute ions, i.e. $Na^+$, $K^+$ and $Ca^{2+}$ in clayey soils are 5.9, 2.0 and 3.7, respectively. In the case of hardened barrier materials, retardation factors are 10% higher than those of clayey soil, which seems to be caused by the increase of the density of the hardened materials and curing.

Effective diffusion coefficients for chloride obtained in this study and those from literature for various materials are compared in Figure 6. The range of effective diffusion for domestic clayey soil located in the western part of Seoul is $2.5–5.5 \times 10^{-10} m^2/s$, which is lower than the range of the effective diffusion coefficients from the literatures. This seems to be caused by the fact that the tested clayey sample has larger fraction of fines than clayey till reported from the foreign literatures has larger fraction of coarse grains, e.g. gravel and sand. Diffusion tests with saline clayey soilsby Duursma (1966) and Shishkina (1966) showed the effective diffusion coefficients in the range, $3.5–5.5 \times 10^{-10} m^2/s$ and $2.4–4.3 \times 10^{-10} m^2/$, respectively. These results are quite similar to the range of effective diffusion coefficient in our study.

Table 6. Summary of effective diffusion coefficients and retardation factors.

| Samples | | chemicals | D* (x $10^{-10}m^2/s$) | | | | R |
|---|---|---|---|---|---|---|---|
| | | | $Cl^-$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | |
| Clayey soil | | NaCl | 4.16 | 0.70 | - | - | 5.94 |
| | | KCl | 2.50 | - | 1.25 | - | 2.00 |
| | | $CaCl_2$ | 5.50 | - | - | 1.50 | 3.67 |
| | | mean | 4.05 | 0.70 | 1.25 | 1.50 | 3.88 |
| Hardened Barrier Materials | PA | NaCl | 1.67 | 0.42 | - | - | 4.00 |
| | | KCl | 0.83 | - | 0.13 | - | 6.70 |
| | | $CaCl_2$ | 2.80 | - | - | 2.10 | 1.33 |
| | | mean | 1.90 | 0.42 | 0.13 | 2.10 | 4.01 |
| | PB | NaCl | 1.94 | 0.33 | - | - | 5.83 |
| | | KCl | 0.50 | - | 0.08 | - | 6.25 |
| | | $CaCl_2$ | 2.20 | - | - | 1.70 | 1.29 |
| | | mean | 1.65 | 0.33 | 0.08 | 1.70 | 4.46 |
| Seal layer | | NaCl | 0.15 | 0.06 | - | - | 2.50 |
| | | KCl | 0.10 | - | 0.03 | - | 3.30 |
| | | $CaCl_2$ | 0.12 | - | - | 0.08 | 1.50 |
| | | mean | 0.12 | 0.06 | 0.03 | 0.08 | 2.43 |

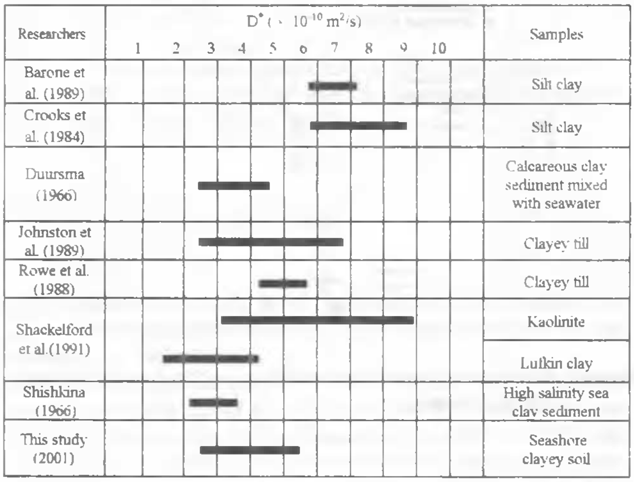

Figure 6. Comparison of diffusion coefficients of Chloride anion for various barrier materials.

## 6 CONCLUSION

The pure diffusion tests are performed in order to analyze diffusive characteristics of inorganic chemicals in clayey soils and hardened barrier materials located under a domestic seashore waste landfill near Seoul, Korea.

The conclusions obtained from the tests are the following:

1) Diffusion coefficient, D*, obtained for chloride in clayey soils ranges in 2.5–5.5 × $10^{-10}$ $m^2/s$ and average D* is 4.0 × $10^{-10}$ $m^2/s$. The retardation factors for reactive solute ions, i.e. $Na^+$, $K^+$ and $Ca^{2+}$, are 5.9, 2.0 and 3.7, respectively.

2) Diffusion coefficient D* of clayey soil with high fraction of fines is lower than that of clayey till which has relatively higher fraction of coarse grains.

3) The average diffusion coefficients of chloride for PA and PB are 1.9 × $10^{-10}m^2/s$ and 1.65 × $10^{-10}m^2/s$, respectively. These values are about 50% less than the diffusion coefficient of tested clayey soil, which seems to be caused by the increase of the density of hardened materials and curing.

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