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Diffusion Anisotropy Through Soft Clay

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Abstract: This study pertains to the quantification of contaminant transport parameters of heavy metal zinc diffusing through saturated soft Bangkok undisturbed clay in the two principal flow directions (vertical direction) perpendicular to and (horizontal direction) parallel to natural bedding marine clay. By using the column tests, the effective diffusion and distribution, D_e and K_d, coefficients were determined by curve fitting to the test data using the POLLUTE software. The results showed that horizontal diffusion is relatively faster (diffusion coefficient higher and distribution coefficients lower) than vertical due to micro-stratifications and loose bond between adjacent layers. Thus, these heterogeneities caused high anisotropy not only in hydraulic conductivity but also in diffusion coefficient and distribution coefficients.

Keywords: Diffusion, Anisotropy, Column test, Retardation, Zinc cation, Soft undisturbed clay liner.

1. INTRODUCTION

As the impact of the toxic chemicals which enter into aquifers is large because of consumption of water by the humans, the clay liners are used as barriers between contaminants and groundwater aquifers to prevent breakthrough of the contaminants into groundwater. The rate of migration of contaminants through the barrier (liner) is essential. The known mechanisms which affect the transport of contaminants through saturated clay barriers are advection (motion of the fluid in soil caused by hydraulic gradient and diffusion caused by chemical concentration gradient and geochemical retardation reactions. As the clays have low hydraulic conductivity and subjected to low hydraulic gradients, advection and dispersion are taken negligible but the main mechanism of transport is diffusion Gillham *et al*., (1984). Clay particles are negatively charged which also trap positive heavy metal cations.

Bergado *et al.* (1990) obtained ratio of horizontal hydraulic conductivity to vertical as 4 to10 for the soft Bangkok clay in his field tests. The anisotropy in hydraulic conductivity is due to particle flatness, orientations, micro-stratification of sedimentary deposits and loose bond between adjacent layers. As there is anisotropy in hydraulic conductivity, there should be anisotropy in diffusion parameters which not mentioned in literature Rowe, *et al*., (1988).

In this study contaminant transport parameters, effective diffusion coefficient and distribution coefficient for heavy metal (zinc) were determined in two the principal flow directions perpendicular (vertical direction) and parallel (horizontal direction) to the natural stratification for undisturbed soft Bangkok clay.

2. Advective-dispersive equation for solute transport

The Shackelford (1989a) the differential equation governing the one-dimensional transient transport of a reactive solute subject to reversible sorption reactions is

$$\partial c/\partial t = \left(D/R_d\right)\left(\partial^2 c/\partial z^2\right) - \left(v_s/R_d\right)\left(\partial c/\partial z\right) \quad \ldots(1)$$

R_d = retardation factor [dimensionless], D_e = effective diffusion coefficient D = coefficient of hydrodynamic dispersion [L^2T^{-1}],

Vs = seepage velocity [LT^{-1}]

2.1 Determination of diffusion coefficient by column method

The diffusion parameters are determined by column method which is also useful when there is an advective component of transport in field situation. Further, in column test, the condition depends on the source concentration of contaminant decrease with time and the contaminant reaches the effluent end of the soil (Shackelford, 1991c).

2.2. The source concentration and decreasing source condition tests

The constant source concentration is the conventional column test in the study of mass transport through the soil.

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(Freeze and Cherry, 1979). After steady-state fluid flow has been established, the fluid in the influent reservoir (usually DDW) is changed to a solution with known concentration, c_o of particular chemical species. The concentration, c of a chemical species in the effluent reservoir is measured over time, and the results are plotted as relative concentration c/c_o vs. time or Pore volumes of flow (PV). The ratio of the pore volumes of flow of the reactive solute to the pore volumes of flow of the non-reactive solute at a relative concentration of 0.5 typically is taken as the retardation factor, R_d (Freeze and Cherry, 1979).

Rowe *et al*., (1988) described the decreasing source concentration with initial concentration of species in the source reservoir which decreases with time. The column consists of a source reservoir, a column of soil, and a porous late (used to collect the effluent from the soil) concentration of the specified chemical species decrease with time in the source reservoir and eventually increased with time in the effluent collection system. The results are plotted as concentration vs. time. A semi-analytical solution of the advective-dispersive transport equation as the computer program, POLLUTE is used to fit theoretical curves to the measured data to determine D_e. At the end of test, the soil is sectioned and the concentration of chemical species is measured as a function of the depth of the soil in the column. Once again, the POLLUTE is used to fit a theoretical curve to the measured concentration profile.

3. MATERIALS AND METHODS

The undisturbed large soil samples of 10 inch diameter of soft Bangkok clay were taken at a depth of 4.0-5.0 m with help of the thin wall cylindrical tubes having internal diameter of 10 inch. For vertical contaminant transport parameters determination, sample was sectioned horizontally in 5 cm thick slices whereas for horizontal transport simulation, sample was sectioned vertically (perpendicular to the direction of natural stratification).

3.1 *Saturation of soil and metal solution*

Clay samples were saturated by soaking method followed by permeation method, prior to start of the diffusion test to minimize mass transport due to the suction in the soil. For the saturation of soil sample DDW was used as a soaking solution. Soil was exposed to moisture controlled room, only from the base to the soaking solution thereby allowing the soaking solution to infiltrate into the soil by capillarity. This process consumed two weeks. Soil was then exposed to the permeation method, for 10 days under hydraulic gradient of 250 in diffusion cells.

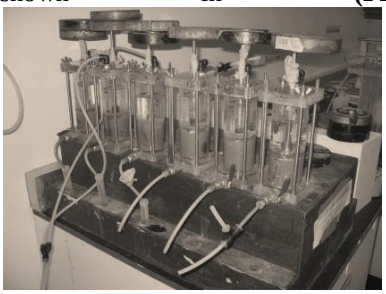
For this study heavy metal solution was used which was made by dissolving chloride salt $ZnCl_2$ in DDW. For Zinc salt the concentration of metal solution was kept 0.001M.

3.2 *Column test*

In decreasing source concentration condition volume of leachate was maintained by adding de-ionized water at the influent end. In constant source concentration condition the source concentration was kept constant by changing the solution after every two days. In case of constant source concentration the effluent volume was collected at a regular interval of one day for each column for chemical analysis while for decreasing source test the influent solution was analyzed on every sixth day.

Sixteen tests were performed with a pure diffusion condition, (i= 0) for three different time periods 30, 48 and 60 days. In vertical direction total fifteen tests were conducted whereas in horizontal direction seventeen tests were performed.

Each model was permeated with specified concentration of salt solution of $ZnCl_2$ under a small head of 6 cm for a certain test period of 15 to 60 days. Each column cell consists of 5 cm inside diameter hollow acrylic cylinder and a hanger weight system to provide good seating of the sample in the column as shown in **(Fig. 1and Fig. 2).**



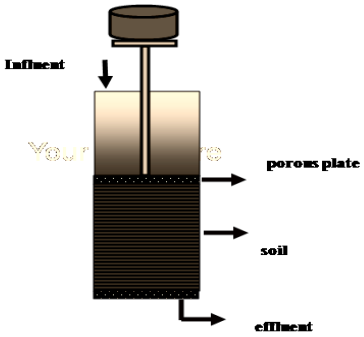
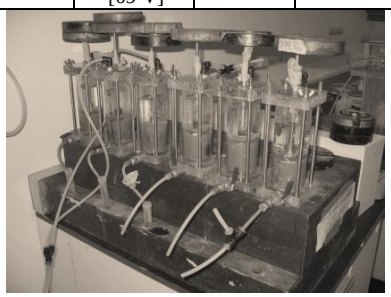


Fig. 1: Column Test setup

Parameter	Source condition	i = 250 t = 30	i = 0		
			t = 30	t = 48	t = 60
D_e (10^{-6} cm^2/sec)	Constant	3.47 [01 V]	2.55 [05 V]	3.01 [06 V]	2.89 [07 V]
		3.70 [02 V]	……..	……..	……..
K_d (cm^3/g)	Constant	15.90 [01 V]	21.80 [05 V]	22.90 [06 V]	24.7 [07 V]
		15.70 [02 V]	……..	…… …	……..
D_e (10^{-6} cm^2/sec)	Decreasing	3.36 [08 V]	2.31 [12 V]	2.66 [13 V]	2.89 [14 V]
		3.36 [09 V]	……..	……..	……..
K_d (cm^3/g)	Decreasing	15.8 [08 V]	21.10 [12 V]	22.40 [13 V]	24.50 [14 V]
		16.1 [09 V]	……..	……..	……..
D_e (10^{-6} cm^2/sec)	Decreasing	3.13 [08 V]	2.20 [12 V]	2.43 [13 V]	2.55 [14 V]
		3.24 [09 V	……..	……..	……..
K_d (cm^3/g)	Decreasing	15.6 [08 V]	20.50 [12 V]	22.00 [13 V]	24.00 [14 V]
		16.0 [09 V]	……..	……..	……..



The soil was sectioned in to the slices (one cm) at the end of the diffusion test and to extract the contaminant species from the soil for chemical analysis. The samples were cut in thickness of one centimetre and extraction of contaminant was carried out by taking 5 grams of wet soil and washing it with 30 ml of DDW. The suspension was centrifuged for 45 minutes at 4000 rpm in centrifuge. Zinc from soil transported though soil during diffusion was determined from the supernatant obtained from centrifuge tube by Spectrophotometer. Inverse of dilution factor was multiplied to convert concentration in DDW to actual concentration of zinc in pore water (Roehl *et al.*, 1998).

3.3 *Semi-analytical simulation of chemical transportation*

The program POLLUTE v 6.3, which directly models column test was applied to fit the theoretical curves to the experimental data for e the contaminant transport parameters D_e and K_d measurement. The diffusion, D_e and distribution, K_d coefficients were found by matching the theoretical curve to the observed drop of concentration with depth and observed drop of concentration in source reservoir with time these parameters can be found.

4. RESULTS

The results are presented in **Ошибка! Источник ссылки не найден.** and Table 2

Table 1 Details of D_e and K_d for Zn^{2+} in vertical direction

02V refers to test No. and vertical direction of test

Table 2 Details of D_e and K_d for Zn^{+2} in horizontal direction

02H refers to test No. and horizontal direction of test

4.1 *Contaminant Transport Parameters in Horizontal (Parallel to the bedding planes)*

(a) Pure diffusion tests under concentration gradient

(i) Constant Source Concentration Condition

For concentration gradient , with zinc transporting though the soil sample effective diffusion co-

Parameter	Source	i = 250 t = 30	i = 0		
			t = 30	t = 48	t = 60
D_e (10^{-6} cm^2/sec)	Constant	6.48 [01 H]	2.66 [05 H]	5.56 [06 H]	5.44 [07 H]
		4.40 [02 H]	……..	……..	……..
K_d (cm^3/g)	Constant	6.60 [01 H]	19.2 [05 H]	12.80 [06 H]	13.60 [07 H]
		14.24			
D_e (10^{-6} cm^2/sec)	Decreasing	[08 H]	[12 H]	[13 H]	[14 H]
		4.05 [09 H]	……..	……..	……..
K_d (cm^3/g)	Decreasing	6.4 [08 H]	19.20 [12 H]	13.30 [13 H]	14.50 [14 H]
		14.21 [09 H]	……..	……..	……..
D_e (10^{-6} cm^2/sec)	Decreasing	6.02 [08 H]	2.55 [12 H]	5.09 [13 H]	4.51 [14 H]
		4.05 [09 H]	……..	……..	……..
K_d (cm^3/g)	Decreasing	6.2 [08 H]	19.1 [12 H]	13.1 [13 H]	14.60 [14 H]
		14.19 [09 H]	……..	……..	……..

efficient, D_e, was in wide range of 2.66-5.56x$10^{-6}$$cm^2$/sec with average of 4.37x$10^{-6}$$cm^2$/sec determined

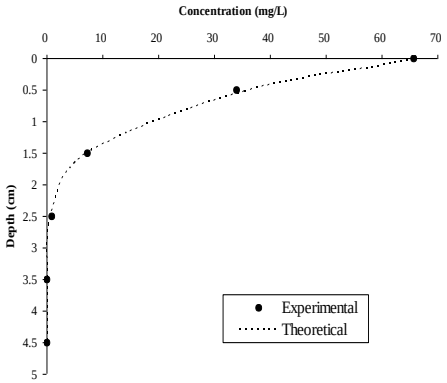


Fig. 3: Constant Source concentration profile with depth for Zn^{2+}

coefficient, K_d, was also in wide range the range of 12.80-19.2 cm^3/g with average of 15.18 cm^3/g. Both diffusion coefficients and distribution coefficients showed increasing trend with increasing testing time similar to the tests in vertical direction.

(i) Decreasing Source concentration Condition

From the depth profile for zinc the effective diffusion coefficient D_e was in the range of *2.66*-$6.13x10^{-6}cm^2/sec$ with an average of $4.68x10^{-6}cm^2/s$. The distribution coefficient, K_d, was in the range of 12.40-19.2 cm^3/g with an average of 14.44 cm^3/g. From source reservoir concentration profile the range for the effective diffusion coefficient is within $2.55\text{-}5.90x10^{-6}cm^2/sec$ with an average of $4.54x10^{-6}$ cm^2/sec. The distribution coefficient, K_d, was in the range of 12.3-19.1 cm^3/g with an average of 14.36 cm^3/g.

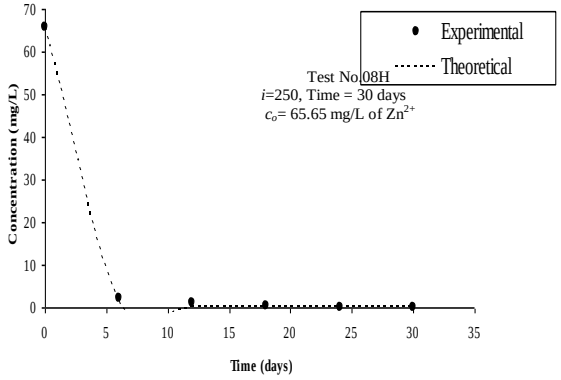
(b) Advection–diffusion tests under hydraulic gradients

(i) Constant Source Concentration Condition

Under the hydraulic gradient of 250 in constant source condition, the diffusion coefficient was in the range of $4.40\text{-}6.48x10^{-6}$ cm^2/sec with an average of $5.44x10^{-6}$ cm^2/sec as determined from the depth profile. The distribution coefficient, K_d, is in the wide range of 6.6-14.24 cm^3/g with an average of 10.42 cm^3/g.

(ii) Decreasing Source Concentration Condition

From the depth profile, with zinc effective diffusion coefficient D_e is in the range of *4.05-6.13*$x10^{-6}cm^2/sec$ with an average of $5.09x10^{-6}cm^2/s$. The distribution coefficient, K_d, is in the range of 6.4-14.21 cm^3/g with an average of 10.31 cm^3/g. From the source reservoir concentration profile as shown in **(Fig. 4),** the range for effective diffusion coefficient was $4.05\text{-}6.02x10^{-6}cm^2/sec$ with an average of $5.04x10^{-6}cm^2/sec$. The distribution coefficient, K_d, was in the range of 6.2-14.19 cm^3/g with average of 10.20 cm^3/g.



The average anisotropy ratio (horizontal to vertical) in diffusion coefficient of heavy metal zinc is in order of 1.75 and 1.54 at zero, 250 gradient respectively. Distribution Coefficient has anisotropy ratio of 0.66 and 0.65 respectively at zero and 250 hydraulic gradient respectively (Almani, 2006).

5. DISCUSSIONS

The test results show different samples showed values in wide range due to micro-stratifications, loose bond between adjacent layers and layers of more permeable material (sand lenses). They showed varying degree of anisotropy not only in hydraulic conductivity but also in diffusion coefficient and distribution coefficients. The diffusion coefficients in non homogenous samples in horizontal direction showed higher values. The diffusion coefficients show increasing trend as hydraulic gradient increases as compared to increasing trend with increase of hydraulic gradient in vertical direction. This anisotropy is essentially due to presence of these layers, loose bond between adjacent layers and layers of more permeable in horizontal direction, particle orientation.

The distribution coefficient is smaller in horizontal direction as compared to vertical direction. This trend is even higher with higher hydraulic gradients. Reason for this increase in diffusion coefficient and decrease in distribution coefficients can be explained from the fact that because of the presence of loose bond between adjacent layers or more permeable sand lenses, contaminants must travel relatively straight paths. On the basis of these findings it can be concluded that horizontal contaminant breakthrough can be earlier and faster as compared to vertical direction.

6. CONCLUSIONS

Based on above study, the conclusions can be drawn.

- The horizontal diffusion is relatively faster (diffusion coefficient higher and retardation factor lower) than the vertical due to micro stratifications, loose bond between adjacent layers and layers of more permeable material (sand lenses).These heterogeneities showed high anisotropy not only in hydraulic Conductivity but also in diffusion coefficient and distribution coefficients.

- The horizontal contaminant breakthrough is earlier and faster as compared to the vertical direction. It can be implied that landfills in excavation or surface impoundments usually their base well below ground

through of these contaminants though vertical walls can be very earlier due to higher advection, diffusion and lower retardation in horizontal direction.

- Compacted clay liners and/or Geomembrane should be provided on sloping sides of landfills to prevent influx of contaminants in horizontal direction to surface streams, fish ponds and agricultural lands nearby these facilities.

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