

Full Length Research Paper

Diffusion coefficient of ions in migration through soil liners

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Contaminant transport through soil liners with low hydraulic conductivity is both by advection and diffusion processes though the diffusion process is dominate. Diffusion coefficient of migrating species has to be considered to calculate the velocity of contaminant plume. Diffusion through a network of clay particles is slower and porous media diffusion coefficient (D_p) is used to consider tortuous flow paths around clay particles by tortuosity factor. Attenuation processes that occur further alter the diffusion coefficient while contaminants travel through the soils. Effective diffusion coefficient (D_e) takes into consideration of attenuation processes. It is known that the cation exchange capacity is an important factor for the attenuation of cationic species. While the normal cation exchange reactions that occur and consequent retardation of cations is well known, very little are known about the effect of anions on retention of cations. The effect of presence of sulphate ions on the effective diffusion coefficient of sodium, which is normally considered as conservative ion, in two different types of soils, has been studied. It has been shown that effective diffusion coefficient of sodium in the presence of sulphate are lower than values reported in literature due to exchange of sodium with calcium ions from the exchangeable complex of clay. Soil with higher cation exchange retains sodium better, making their migration much lower.

Key words: Cation exchange capacity, clays, diffusion coefficient, hydraulic conductivity, porous media.

INTRODUCTION

The release of the contaminants into the environment is inevitable. The release and migration of contaminants such as chemicals, pesticides, nutrients etc. in run-off from industrial, agricultural and other lands is both an economic loss and a severe threat to the quality of surface water and ultimately the ground water. Contaminants are released by manufacture and use of products and as a result of treatment and disposal of wastes, by accident, by neglect and so on. Upon release to the environment, contaminants move and respond to a number of interrelated natural and manmade factors. They may move quickly or ever so slowly to the ground water in their original or altered form. Usually contaminant

transport in porous media is controlled by a variety of physical, chemical and biological processes (Freeze and Cherry, 1979; Daniel and Shackelford, 1991).

The physical process includes diffusion, advection and dispersion. The chemical process usually includes sorption, dissolution precipitation, complexation, hydrolysis/substitution and oxidation. Mathematical models are available to calculate the rate of migration of a given species considering advection alone or diffusion alone as the only process. In many field situations, migration occurs in response to both to advection and diffusion. The relative contributions from these processes depend on the hydraulic conductivity of the media to fluid. At high hydraulic conductivity, the contribution from diffusion becomes negligible. As the hydraulic conductivity becomes less, the contribution from diffusion increases. At relatively very low hydraulic conductivity, diffusion becomes main process for contaminant migration.

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However often it is necessary to consider the combined effect of advection and diffusion as migration through compacted clay liners. It may also be necessary the transport of contaminants by diffusion alone.

Calculation of breakthrough times

Considering diffusion alone as responsible for migration of contaminating ions, the variation of relative concentration with time through a soil column can be calculated using the following equation,

$$\frac{C}{C_0} = \frac{1}{2} \operatorname{erfc}\left(\frac{X}{2\sqrt{D_e t}}\right)$$

where, $\frac{C}{C_0}$ = ratio of effluent concentration to influent concentration; D_e = effective diffusion coefficient of contaminating species; x = thickness of the column, and t = time.

Considering both advection and diffusion as responsible for migration of contaminating ions, the variations of relative concentrations of ions with time is calculated using the equation,

$$\frac{C}{C_0} = \frac{1}{2} \left[\operatorname{erfc}\left(\frac{Z - v_s t}{2\sqrt{(D_e t)}}\right) + \exp\left(\frac{R v_s Z}{D_e}\right) \operatorname{erfc}\left(\frac{Z + v_s t}{2\sqrt{(D_e t)}}\right) \right]$$

where, $\frac{C}{C_0}$ = ratio of effluent concentration to influent concentration; D_e = effective diffusion coefficient of contaminating species; Z = thickness of the column; t = time; v_s = Seepage velocity of pore fluid, and R = retardation factor

For plotting the variation of relative concentration (C/C_0) with time, experimentally determined value of D_e (Diffusion co-efficient) is used.

From the previous discussion, it is obvious the molecular coefficient plays an important role in the relative velocities of different molecules in a given media. The molecular diffusion coefficient is a fundamental property of the chemical and the solvent (water). Molecular diffusion coefficients are tabulated for many chemicals in water in Handbooks of Chemistry and Physics, which are estimated from chemical and thermodynamic properties. The rate of diffusion is sensitive to a number of parameters. Maximum rates of migration by diffusion occur in bulk or free water at extreme dilution. Free solution diffusion coefficient (D_0) would normally represent these maximum values. The rate of chemical movement or mass flux through a soil may be slower than by diffusion in pure water. Diffusion through a network of clay particles involves the diffusive movement of the species of interest in the pore water between clay particles. The tortuosity factor accounts

for the increased distance of transport and the more tortuous pathways experienced by solutes diffusing through porous media. Porous media diffusion coefficient (D_p) takes into consideration of tortuosity factor (Rowe et al., 1995; Sharma and Lewis, 1994). The porous system diffusion coefficient D_p can be calculated from Fick's law by

$$D_p = D_0 W_T = \theta D_e$$

in which W_T is complex tortuosity factor, D_0 is free solution diffusion coefficient; θ is volumetric water content;

$$W_T = \alpha_{ff} \gamma_e \left(\frac{L}{L_e}\right)^2 D_0 = \tau D_0$$

$$\tau = \alpha_{ff} \gamma_e \left(\frac{L}{L_e}\right)^2$$

where α_{ff} is the decreased fluidity factor related to adsorbed double layer factor; γ_e is the electrostatic interaction factor; $(L/L_e)^2$ is the geometric tortuosity factor and τ is the tortuosity factor for the clay.

The rate of migration of species is further affected by retardation and attenuation processes that take place during their migration in the soil media.

Retardation attenuation processes

Attenuation of leachate occurs in two stages. In the first stage, soil in the unsaturated zone reacts with the leachate constituents and attenuates the leachate in part. The second stage of attenuation occurs in the ground water aquifer.

Adsorption

Adsorption is the process by which molecules adhere to the surface of individual clay particles. Because of difficulty in distinguishing adsorption from exchange reactions experimentally, it is sometimes referred to as adsorption-exchange reactions. However there is a basic difference between adsorption and exchange reactions.

Biological uptake

Biological uptake is a mechanism by which microorganisms either break down or adsorb constituents and thereby attenuate leachate. Microbial growth in soil systems can have a tremendous impact on leachate attenuation initially.

Cation and anion exchange

The exchange reactions mainly involve the clay minerals and may be defined as exchange of ions of one type of ions by another type without disturbing the mineral structure. The solid phase of a given soil may contain various amounts of crystalline clay and non clay minerals, non crystalline clay minerals, organic matter and salts. Although the amount of non clay minerals in a given soil is usually greater than the proportion of clay minerals present, cation exchange performed by the clay mineral fraction is quite significant. For the soils used in barrier system, the cation exchange capacities are quite large. The cation exchange capacities of soils are expressed as meq/100 g of soil.

Precipitation

Chemical precipitation involves a phase in which dissolved chemical species are crystallized and deposited from a solution because, their total concentration exceeds their solubility limit. The solubility limits depend on factors such as ionic species and their concentration, temperature, pH, redox potential and concentration of dissolved substances.

Effect of attenuation processes on diffusion coefficients

The contaminant transport through the soils may be retarded through processes of sorption, precipitation, biodegradation, and filtration. The attenuation processes included are: Cation removal, anion removal, and biodegradation. The important process for sorption of cations is by ion exchange at exchange sites and in the inter layers of clays. The rate of leakage will depend on the diffusion coefficients of ions and the permeability of the clay liners to the given leachate. While dilute solutions of inorganic chemical change the clay permeability, dilute solutions of organic chemicals have virtually no effect. Hence the contaminant migration through the soil depends greatly on the diffusion coefficients of migrating ion. Also it was observed that the leachates generated in normal municipal landfill have no significant influence on the permeability of the clay liners. Hence the contaminant migration through the given clay liner depends greatly on the diffusion coefficients of migrating ion. Diffusion of species of interest in pore water between the clay particles is a complicated process.

Effective diffusion coefficient (D_e) takes into consideration other attenuation processes. However, the difference between porous media diffusion coefficient and effective diffusion coefficient is very little for conservative ions like chloride. Determination of diffusion coefficients of some common ions is important in estimating the total

Breakthrough times. Column tests are usually employed (Shackelford, 1991) to determine the diffusion coefficient. Diffusion coefficients are determined from the breakthrough curves plotted using column test data. It has been brought out that the cation exchange capacity of soil plays an important role in the attenuation of cations. Either to sodium ion is considered as conservative ion because normally sodium cannot replace other exchangeable ions of soil and adsorbed on to the clay surface. Barone et al. (1988) have shown that the adsorption of sodium and potassium is affected by other exchangeable ions in the leachate. It is not known how the effective diffusion coefficient (D_e) of sodium is altered in the presence of these ions. Knowing the effective diffusion coefficient (D_e), it is possible to calculate the rate of migration of a species using the aforementioned equation.

Scope of the present work

It is proposed to determine the breakthrough times of two soils (red earth and brown earth) for a given thickness which are used as liners after proper compaction in the migration of Sodium and Sulphate ions. The contaminant migration through the given clay liner depends greatly on the diffusion coefficients of migrating ions. This study proposed to determine the diffusion coefficients of sodium and sulphate ions while migrating through two types of soil liners. One of the most acceptable methods of determining diffusion coefficient is by column experiment. Thus, it is proposed to determine them for ions by performing column experiments. The column experiments are conducted on two compacted soils – red earth and brown earth. From the data obtained by column experiments and using Ogata-Bank's equation, the values of effective diffusion coefficients of individual ions sodium and sulphate are calculated. The variation of relative concentration with time is discussed under two conditions of contaminant migration processes, that is, (i) contaminant migration with diffusion alone; (ii) contaminant migration with advection and diffusion. For each condition, the variation of relative concentration of different ions with time are plotted for two soil types by taking experimental values of diffusion coefficients and then they are compared with the same plots prepared by taking literature values of diffusion coefficients. The breakthrough times are reported corresponding to relative concentration of 0.5.

MATERIALS

Brown earth

Brown earth obtained from a construction site on airport road in Bangalore was used in this study. The sample was collected by open excavation from a depth of 1 m from natural ground. The soil

Table 1. Index and physico chemical properties of soils used.

Property	Brown earth	Red earth
Specific gravity	2.63	2.64
Liquid limit (%)	67.5	38.0
Plastic limit (%)	23.2	21.0
Shrinkage limit (%)	13.4	18.0
Max dry density (g/cm ³)	1.63	1.68
Optimum moisture content (%)	27.5	19.2
Cation exchange capacity (meq/100g)	33	18

was dried and passed through IS 425-micron sieve. The soil so obtained has clay content of 55%. The clay content consisted predominantly of Kaolinitic mineral. The cation exchange capacity of the soil is about 33-meq/100 g.

Red earth

Red earth used in this study was obtained from Indian Institute of Science campus, Bangalore. The soil was collected by open excavation from a depth of 1 m from the natural ground. The soil was dried and passed through IS 425-micron sieve. The clay so obtained has clay content of 38%. The clay content consisted predominantly of Kaolinitic mineral. The cation exchange capacity of the soil is about 18-meq/100 g. The properties of both the soils used are presented in Table 1.

EXPERIMENTAL SET UP FOR SOIL COLUMN TEST

The apparatus used in this study was designed such that both diffusion and advective-diffusion tests could be performed (Figure 1). The experimental set up consists of following four major components namely: (i) Influent reservoir; (ii) Pressure system; (iii) Column assembly, and (iv) Effluent collector.

Influent reservoir

It consists of a tank made of glass or polyethylene with two opening. One at the top for transferring the synthetic source solution of interest into, and the other at the bottom to allow it migrate through the soil specimen. The solution of interest is placed in this influent reservoir and is stirred at frequent intervals so as to maintain constant initial concentration.

Pressure system

Pressure is applied so as to simulate field condition when the pressure is translated into hydraulic gradient. Also application of pressure reduces the testing duration for the column experiments, which may otherwise take number of years to give breakthrough results. Pressure gauge is connected to the influent reservoir and to the column assembly. A uniform pressure of 15 kPa is maintained throughout the experimental period by controlling the flow rate from the influent reservoir.

Column assembly

The column assembly consists of Plexiglas cylinder of 32 cm long,

9.2 cm inner diameter and 0.5 cm thick. The Plexiglas cylinder is attached to the base plate which houses a filter paper and a porous stone as shown in the Figure 4. The soil specimen is uniformly compacted to a height of 30 cm. After the sample is compacted, one more set of porous stone and filter paper are placed at the top and capped with top plate as shown in the figure. The influent line is connected at the bottom of the column assembly and effluent line at the top to collect the effluent.

Effluent collector

It consists of a measuring jar covered at the top so as to avoid evaporation of collected leachate. The effluent collected in the collector is monitored regularly.

Preparation of sodium sulphate solution

About 3.086 g of Na₂SO₄ was weighed accurately and dissolved in water and made upto one litre in volumetric flask. Knowing the exact weight of the salt, the concentrations of ions are calculated. The solution prepared for the study contained about 1000 ppm of sodium and 2088 ppm of sulphate.

EXPERIMENTAL PROCEDURE

Sample preparation and placement in the column

The oven dried soils of Red Earth and Brown Earth of required quantity was mixed with necessary amount of water separately so as to prepare sample of required density. Soils were compacted to a dry density of 0.85 times of Proctor's maximum dry density at water content 2% lower than optimum water content. The soils were mixed thoroughly and kept in polythene bag in a humid desiccator overnight to achieve uniform moisture content. The soil was then compacted to the required density by dividing the soil into 3 equal parts by weight and then, each part is compacted into the (specimen) Plexiglass cylinder, one by one using a screw jack to ensure uniform compaction for the entire specimen.

Monitoring the effluent

The volume of the effluent that comes out of the column with time was monitored at regular intervals and the concentration of different ions measured. The interval selected varied with flow rate. Column experiments usually take considerably long duration for breakthrough. Under conditions maintained for the experiments, each column experiments with brown earth took nearly 6 to 7 months and with red earth about 4 months. The test is terminated

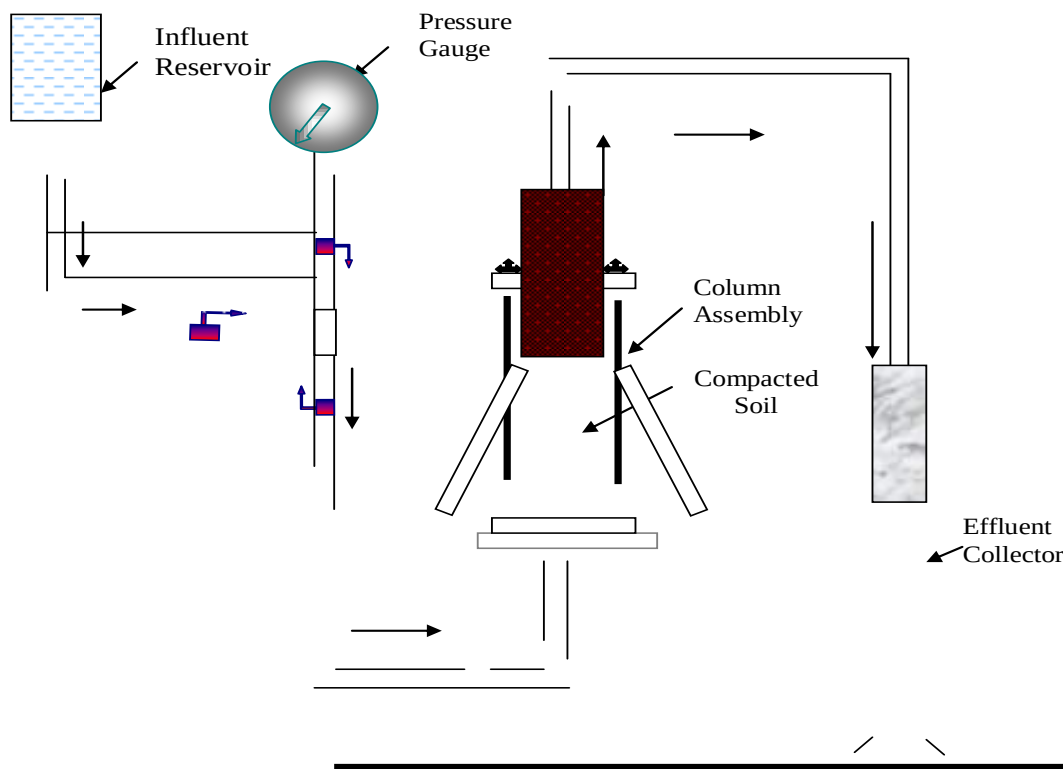


Figure 1. Grouping.

Table 2. Experimental values of effective diffusion coefficients of ions (m^2/s).

Ion	Red earth	Brown earth
Sodium	7.995×10^{-10}	2.771×10^{-10}
Sulphate	4.136×10^{-10}	3.116×10^{-10}

when the effluent concentration reaches influent concentration ($C = C_0$).

Determination of effective diffusion coefficients

In order to obtain the values of effective diffusion coefficients, a plot of relative concentration versus time or number of pore volume are plotted. From the plot, the time ($t_{0.16}$) corresponding to $C/C_0 = 0.16$ and time ($t_{0.84}$) corresponding to $C/C_0 = 0.84$ are obtained. Using these values and knowing the thickness of liner (L) and knowing the value of velocity, effective diffusion coefficient was calculated using the following Ogata Bank's equation

$$\frac{C}{C_0} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{1-U}{2\sqrt{UD_e/vL}} \right) \right]$$

where, $U = v n A t / A L n = v t / L$

$J_{0.84} = [(U-1) / U^{1/2}]$ when $C/C_0 = 0.84$

$J_{0.16} = [(U-1) / U^{1/2}]$ when $C/C_0 = 0.16$

The simplified solution to the aforementioned equation will be as follows

$$D_e = \frac{vL}{8} [U_{0.84} - J_{0.16}]^2$$

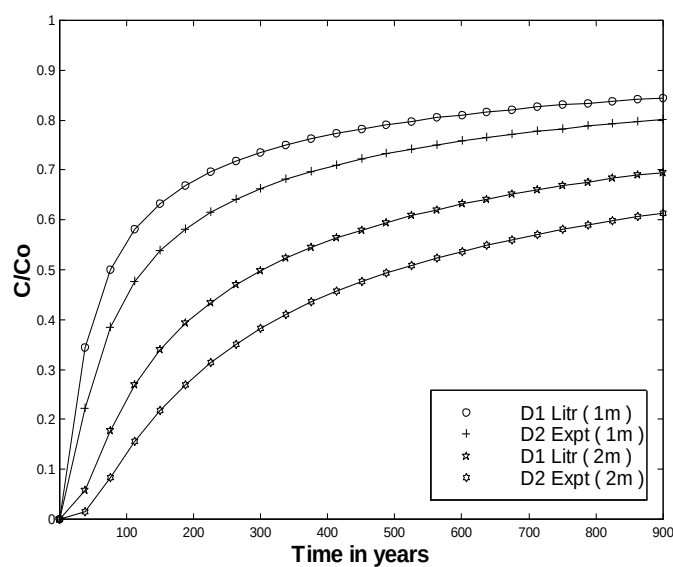
The column tests are conducted on two types of compacted soils - red earth and brown earth - using sodium sulphate as single salt solution and sodium chloride and calcium chloride in multi salt solution as leachates. From the data obtained from column experiments and using Ogata Bank's Equation, the values of effective diffusion co-efficient for each ion are calculated.

It has been found from earlier studies conducted that the contaminant migration through porous media can be modeled and knowing soil parameters and diffusion coefficients of ions, the breakthrough times (under diffusion) and hence the effective performances of liners can be calculated. The migration of ions by diffusion and with advection can be modeled if the seepage velocities of the contaminant leachate are known. The effective diffusion coefficients of individual ions, that is, sodium and sulphate in red earth and brown earth obtained from column experiments are summarised in Table 2.

This paper is proposed to generate the theoretical contaminant

Table 3. Values of porous media diffusion coefficients (Hill, 1984; Samson et al., 2003).

Ion	Porous media diffusion coefficient (m^2/s)
Sodium	4.6×10^{-10}
Sulphate	2.0×10^{-10}

**Figure 2.** Variation of relative concentration of sodium with time for different diffusion coefficients in brown earth

migration curves using available numerical models and taking the values of effective diffusion co-efficients determined under different conditions.

RESULTS AND DISCUSSION

Contaminant migration with diffusion alone

Variation of relative concentration for various ions with time

For plotting the variation of relative concentration (C/C_0) with time, appropriate D_e (Diffusion co-efficient) is substituted for different chemical species considering ($x = 1 \text{ m}, 2 \text{ m}$) thickness of liner as 1 and 2 m. A computer programme developed using MATLAB-5.2 is used. The variation of C/C_0 with time with effective diffusion coefficient determined for 1 and 2 m thickness is plotted for red earth and brown earth separately and then compared. In addition to these, the variation of relative concentration with time considering diffusion co-efficient values most commonly reported in the literature are also considered for comparison along with the graphs. These values for individual ions are summarized in Table 3.

Ion migration in different soils

Figure 2 shows the variation of relative concentration of sodium with time for different diffusion co-efficients - diffusion coefficient reported in literature and the effective diffusion coefficient obtained from experiment - in Brown earth considering 1 and 2 m thickness of liner. It can be seen that the curve is S-shaped and it can be observed that generally with any diffusion coefficient, the relative concentration increases with time. There can be infinite number of transit times depending on particular choice of relative concentration. The usual practice is to define transit time or breakthrough time as the time corresponding to relative concentration, C/C_0 of 0.5. As the thickness of liner increases break through time also increases. The curve showing variation of relative concentration of sodium with time for experimentally obtained diffusion coefficient obtained in the study lies below that of the literature diffusion coefficient. This as explained earlier is due to retention of sodium in the ion exchange complex of the clay by replacing calcium ions. Thus break through time of sodium in brown earth in the presence of sulphate is much higher. Thus it can be observed that, for the proposed liner for 1 m thickness of liner $C/C_0 = 0.5$ the breakthrough cannot occur before 120 years and for 2 m thick liner $C/C_0 = 0.5$ before 515 years. The corresponding breakthrough times with literature diffusion coefficients are 90 and 300 years for 1 and 2 m thickness of liner. Thus the present study shows that the proposed brown earth liner can safely be used 120 years with 1 m thickness and 515 years with 2 m thickness before the breakthrough of sodium ions occur.

Figure 3 shows the variation of relative concentration of sodium with time for different diffusion co-efficient in red earth considering 1 and 2 m thickness of liner. From the graph, it can be observed that with any diffusion coefficient, the relative concentration increases with time and all the curves are S-shaped. As the thickness of liner increases break through, time also increases. The curve showing variation of relative concentration of sodium with time for experimentally obtained diffusion coefficient in the study lies slightly above that of the literature diffusion coefficient. However the break through time of sodium in red earth in the presence of sulphate is slightly lower than literature values. Thus for the red earth liner for 1 m thickness of liner, the break through ($C/C_0 = 0.5$) times are 120 and 190 years for 1 and 2 m thickness, respectively. The breakthrough times for red earth are lower than obtained using diffusion coefficients from literature values of 90 and 300 years for 1 m.

Figure 4 shows the variation of relative concentration of sulphate with time for different diffusion co-efficient in brown earth considering 1 and 2 m thickness of liner. From the graph, it can be observed that with any diffusion coefficient, the relative concentration increases with time and the curves are S-shaped. As the thickness of liner increases break through, time also increases. The curve

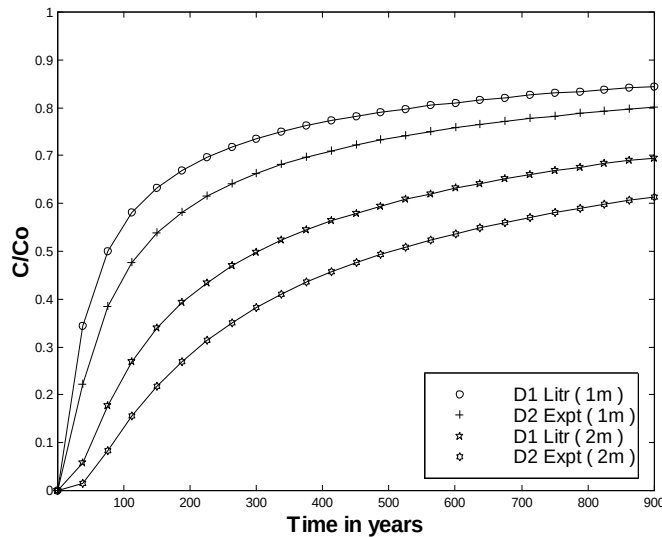


Figure 3. Variation of relative concentration of sodium with time for different diffusion coefficients in red earth.

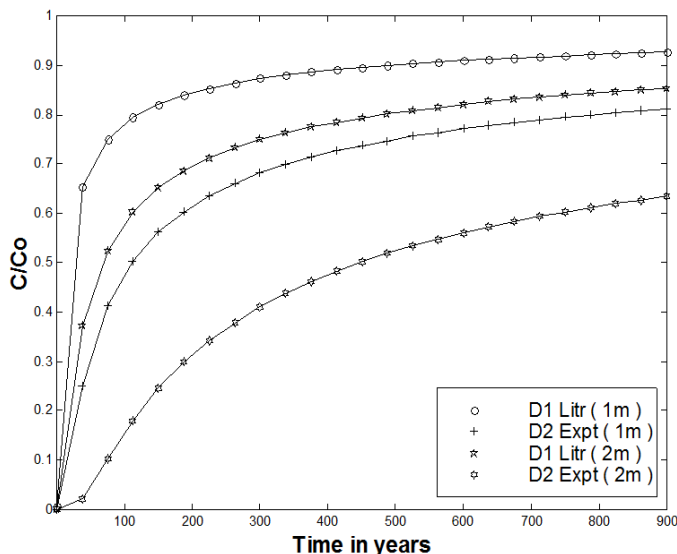


Figure 4. Variation of relative concentration of sulphate with time for different diffusion coefficients in brown earth.

showing variation of relative concentration of sulphate with time for experimentally obtained diffusion coefficient obtained in the study lies above that of the literature diffusion coefficient. Thus the break through time of sulphate ion in brown earth in the presence of sodium ions is lower. This can be observed in that for the proposed liner, for 1 m thickness of liner the break through ($C/C_0 = 0.5$) can occur in about 105 years and for 2 m thick liner in about 450 years as compared to the breakthrough times of 175 and 675 years for 1 and 2 m thickness, respectively with the reported literature values. Thus the proposed Brown earth liner can only be safely

be used for 105 and 450 years with 1 and 2 m thickness, respectively.

Figure 5 shows the variation of relative concentration of sulphate with time for different diffusion co-efficient in red earth considering 1 and 2 m thickness of liner. Again the relative concentration increases with time and the curves are S-shaped. As the thickness of liner increases break through, time also increases. The curve showing variation of relative concentration of sulphate with time for experimentally obtained diffusion coefficient obtained in the study lies very close to the curve obtained for the literature diffusion coefficient. The breakthrough times reported in the literature values and effective diffusion coefficient determined in the study is comparable. Thus for red earth liner for 1 m thickness the break through ($C/C_0 = 0.5$) cannot occur before 95 years and for 2 m thick liner $C/C_0 = 0.5$ before 340 years.

Comparing Figures 2 to 5, it can be concluded that the breakthrough time for brown earth are about the same for sodium and sulphate whereas for red earth breakthrough with sodium is about half the time for sulphate.

Relative performances of red earth and brown earth for migration of ions

Figure 6 shows the variation of relative concentration of sodium with time for different diffusion co-efficient in brown earth and red earth considering 1 and 2 m thickness of liner. The curve showing variation of relative concentration of sodium with time determined experimentally lies below that obtained from literature value in brown earth and vice versa in red earth. This is due to the higher CEC of brown earth there by retarding sodium. Hence break through time for sodium ions for brown earth is higher than the break through time in red earth. Thus for 1 m thickness of brown earth liner the break through ($C/C_0 = 0.5$) cannot occur before 120 years in brown earth liner and 50 years in red earth liner. For 2 m thickness of liner the breakthrough ($C/C_0 = 0.5$) time for brown earth cannot occur before 515 and 190 years in red earth. Thus the proposed brown earth liner is having higher design life compared to red earth.

Figure 7 shows the variation of relative concentration of sulphate with time for different diffusion co-efficient in brown earth and red earth considering 1 and 2m thickness of liner. The curves showing variation of relative concentration of sulphate with time for both the soils determined experimentally lie only slightly above the curves with literature value and hence the break through times are only slightly lower than the values obtained with literature values. Thus for 1 m thickness of liner, the break-through cannot occur before 105 years in brown earth liner and 95 years in red earth liner. For 2 m thick liner, the breakthrough cannot occur before 450 years in brown earth and 340 years in red earth. Thus the brown earth even for sulphate ions. $C/C_0 = 0.5$ cannot occur before 30 h liner is having higher design life compared to

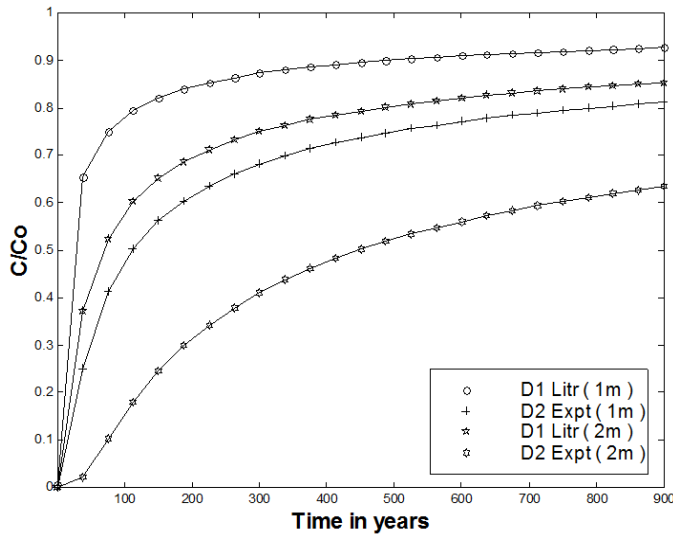


Figure 5. Variation of relative concentration of sulphate with time for different diffusion coefficients in red earth.

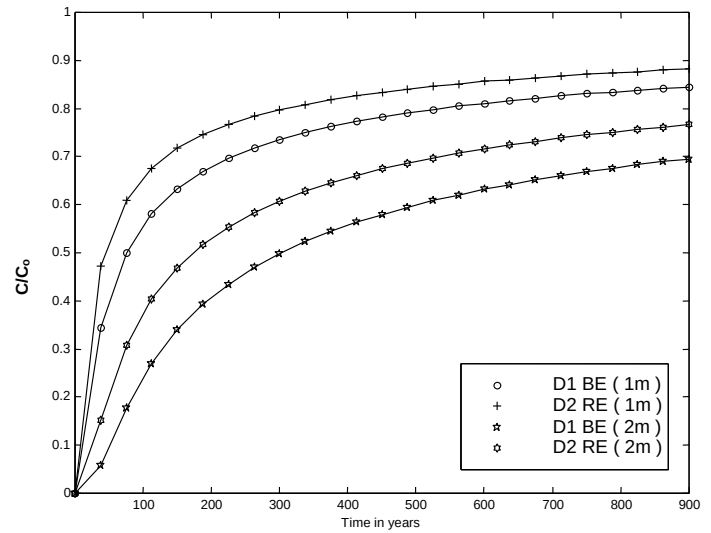


Figure 7. Variation of relative concentration of sulphate with time for different diffusion coefficients in red earth and brown earth.

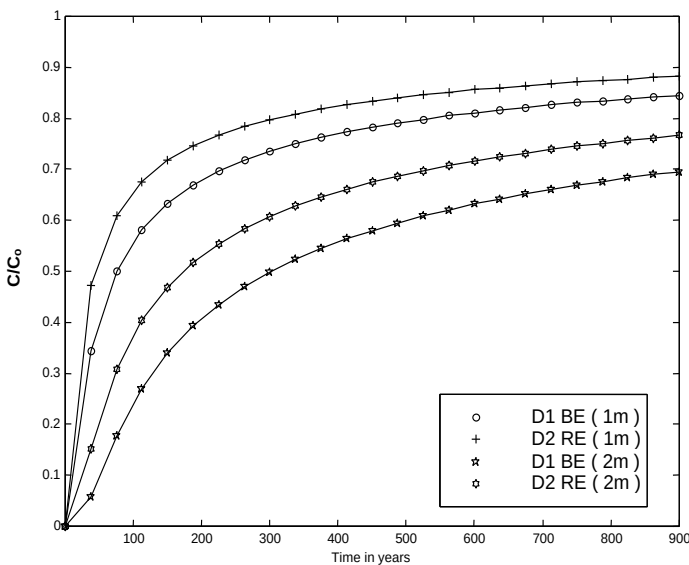


Figure 6. Variation of relative concentration of sodium with time for different diffusion coefficients in red earth and brown earth.

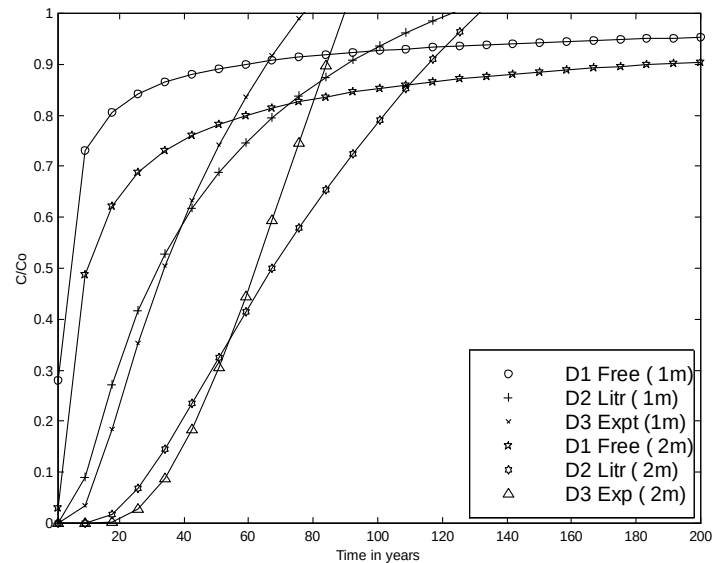


Figure 8. Variation of relative concentration of sodium with time with advection and with different diffusion coefficients in brown earth.

red earth years in red earth liner and 52 years in brown earth liner. For 2 m thick liner, $C/C_0 = 0.5$ cannot occur before 235 years in brown earth and 115 years in red earth. The break through times for sodium and sulphate is higher in brown earth than for red earth. This is because of higher cation exchange capacity and higher specific surface of brown earth than for red earth.

Contaminant migration with advection and diffusion

The variation of C/C_0 with time for 1 and 2 m thickness is

plotted for red earth and brown earth separately and then combined results are also presented. In addition to these, the variation of relative concentration with time considering diffusion co-efficient values (most commonly obtained) from the literature is also presented for comparison along with the graphs.

Ion migration in different soils

Figure 8 shows the variation of relative concentration of sodium with advection and with different diffusion

Table 4. Comparison of breakthrough times of different chemical species considering diffusion alone; and advection and diffusion.

S/N	Break through time at C/Co = 0.5 (Years)	Brow earth		Red earth	
		Diffusion alone	Advection and diffusion	Diffusion alone	Advection and diffusion
A. For 1 m thick liner					
1	Sodium with Sulphate	120	35	50	30
2	Sulphate	105	37	95	36
B. For 2 m thick liner					
1	Sodium with Sulphate	515	63	190	65
2	Sulphate	450	62	340	64

co-efficients - free solution diffusion coefficient, diffusion coefficient reported in literature and the effective diffusion coefficient obtained from experiment - in brown earth considering 1 and 2 m thickness of liner. It is seen from Table 4 that the break through times increases steeply from 1 to 2 m thickness of liner because of nature of breakthrough times which increase steeply for a particular thickness. It can be seen that the curve is S-shaped and it can be observed that generally with any diffusion coefficient, the relative concentration increases with time. There can be infinite number of transit times depending on particular choice of relative concentration. The usual practice is to define transit time or breakthrough time as the time corresponding to relative concentration, C/C_0 of 0.5. As the thickness of liner increases, break through time also increases. However, breakthrough curve with experimentally obtained diffusion coefficient is slightly below the curve obtained with diffusion coefficient reported in literature. Beyond C/C_0 of 0.5, the breakthrough curve obtained with experimentally determined diffusion coefficient is above that of the curve obtained with reported diffusion coefficient. The consequence of this behavior is that the breakthrough time for C/C_0 of 0.5 are very nearly the same for both values of diffusion coefficient. Thus the effect of advection masks the effect of variation in diffusion coefficient. However the breakthrough time for C/C_0 of 1.0 is much lower for case using lower diffusion coefficient. The curve showing variation of relative concentration of sodium with time for experimentally obtained diffusion coefficient obtained in the study lies close to that of the literature diffusion coefficient. However the curve with experimentally determined lower diffusion coefficient crosses the curve obtained with diffusion coefficient taken from literature for higher values of C/C_0 . The curve even crosses that obtained with free diffusion coefficient. Similar results were also obtained by Quigley et al. (1988) in their assessment of clay barriers for impoundment of domestic leachate. Thus it can be observed that, for the proposed liner for 1 m thickness of liner $C/C_0 = 0.5$ the breakthrough cannot occur before 35 years and for 2 m thick liner $C/C_0 = 0.5$ before 63 years. The corresponding breakthrough times with literature

diffusion coefficients are 36 and 68 years for 1 and 2 m thickness of liner. Thus the present study shows that the proposed brown earth liner can safely be used 35 years with 1 m thickness and 63 years with 2 m thickness before the breakthrough of sodium ions occur.

Figure 9 shows the variation of relative concentration of sodium with advection and with different diffusion coefficients in red earth considering 1 and 2 m thickness of liner. From the graph, it can be observed that relative concentration increases with time and the curve is S-shaped. As the thickness of liner increases, break through time also increases. However, breakthrough curve with experimentally obtained diffusion coefficient is slightly above the curve obtained with diffusion coefficient reported in literature. Beyond C/C_0 of 0.5, the breakthrough curve obtained with experimentally determined diffusion coefficient is below that of the curve obtained with reported diffusion coefficient. The consequence of this behavior is that the breakthrough time for C/C_0 of 0.5 are very nearly the same for both values of diffusion coefficient. Thus the effect of advection masks the effect of variation in diffusion coefficient. The smaller differences between diffusion coefficients are much more effectively masked than in the case of brown earth. Thus it can be observed that, for the proposed liner of 1 m thick, breakthrough occurs at 30 years and for 2 m thick liner breakthrough occurs at 65 years. Also the equilibrium concentration, that is, $C/C_0=1.0$ considering 1 m thick liner occurs at 95 years and at 220 years for 2 m thick liner, respectively.

Figure 10 shows the variation of relative concentration of sulphate with advection and with different diffusion coefficients in Brown earth considering 1 and 2 m thickness of liner. From the graph, it can be observed that relative concentration increases with time and the curve is S-shaped. As the thickness of liner increases, break through time also increases. However breakthrough curve with experimentally obtained diffusion coefficient is slightly above the curve obtained with diffusion coefficient reported in literature. Beyond C/C_0 of 0.5, the breakthrough curve obtained with experimentally determined diffusion coefficient is below that of the curve obtained with reported diffusion coefficient. The consequence of

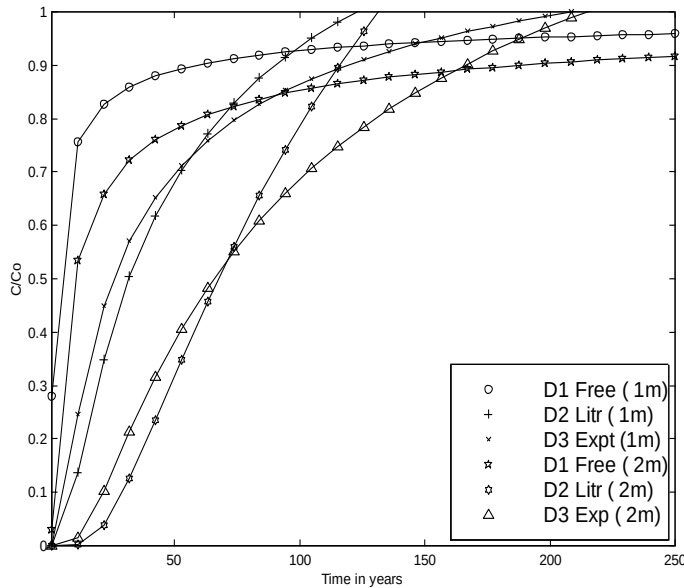


Figure 9. Variation of relative concentration of sodium with time with advection and with different diffusion coefficients in red earth.

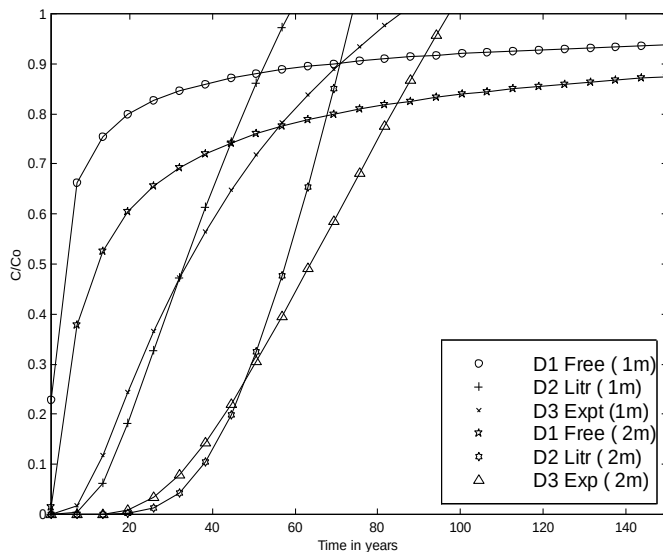


Figure 10. Variation of relative concentration of sulphate with time with advection and with different diffusion coefficients in brown earth.

this behavior is that the breakthrough time for C/C_0 of 0.5 are very nearly the same for both values of diffusion coefficient. Thus the effect of advection masks the effect of variation in diffusion coefficient. The smaller differences between diffusion coefficients are much more effectively masked than in the case of brown earth. Thus it can be observed that, for the proposed liner of 1m thick, breakthrough occurs at 37 years and for 2 m thick liner breakthrough occurs at 62 years. Also the equilibrium

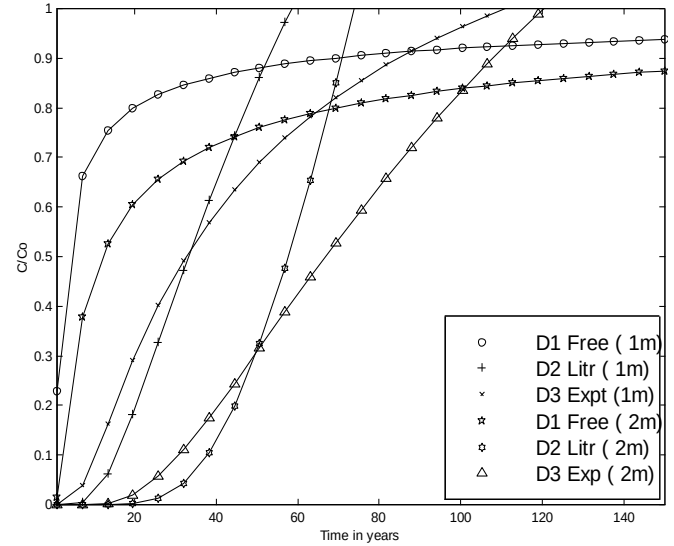


Figure 11. Variation of relative concentration of sulphate with time with advection and with different diffusion coefficients in red earth.

concentration ie $C/C_0=1.0$ considering 1 m thick liner occurs at 85 years and at 96 years for 2 m thick liner respectively.

Figure 11 shows the variation of relative concentration of sulphate with advection and with different diffusion coefficients in red earth considering 1 and 2 m thickness of liner. From the graph, it can be observed that relative concentration increases with time and the curve is S-shaped. As the thickness of liner increase break through, time also increases. However breakthrough curve with experimentally obtained diffusion coefficient is slightly above the curve obtained with diffusion coefficient reported in literature. Beyond C/C_0 of 0.5, the breakthrough curve obtained with experimental diffusion coefficient is below that of the curve obtained with reported diffusion coefficient. The consequence of this behavior is that the breakthrough time for C/C_0 of 0.5 are very nearly the same for both values of diffusion coefficient. Thus the effect of advection masks the effect of variation in diffusion coefficient. The smaller differences between diffusion coefficients are much more effectively masked than in the case of brown earth. Thus it can be observed that, for the proposed liner of 1 m thick, breakthrough occurs at 36 years and for 2 m thick liner breakthrough occurs at 64 years. Also the equilibrium concentration, that is, $C/C_0 = 1.0$ considering 1 m thick liner occurs at 110 years and at 120 years for 2 m thick liner respectively.

Conclusions

The following conclusions are drawn:

1. For a given thickness of the liner, the break through

time of sodium ion is more than that of sulphate ions. Also the differences in breakthrough times of sodium ion in soils are more compared to sulphate ions.

2. While sodium is retarded in both the soils to a certain extent, sulphate is not retarded in either of the soils studied.

3. The breakthrough times for brown earth with sodium and sulphate ions are about the same whereas for red earth the breakthrough time with sulphate is half of that with sodium.

4. The breakthrough times of ions of brown earth and red earth are about the same under the processes of advection and diffusion. Thus the effect of variation in diffusion coefficients is masked by advection.

FUTURE DIRECTION FOR THE WORK

The effect of interferences of other ions on the diffusion coefficients of other ions present in actual effluent needs to be studied for selection of thickness of liner.

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