SALT DIFFUSION IN COMPACTED PLASTIC CLAY: EXPERIMENTAL AND THEORETICAL EVALUATION

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Abstract: In this paper, experimental results of diffusion transport of salt through compacted, saturated bentonite clay was presented. Two different diffusion techniques namely, through-diffusion and half-cell method were used to obtain diffusion and retention characteristics of the bentonite specimen which has a potential application as a liner material in engineered landfills and backfill material in high-level nuclear waste repository. The experiments were carried out on duplicate specimens subjected to the same initial compacted density and concentration gradient to understand the underlying mechanism of both the experimental techniques. A graphical user interface (GUI) based on Dot-Net application, CONTRADIS, was utilized to estimate the model parameters by inverse analysis on the experimental data. The GUI utilizes the analytical solutions for analyzing the data obtained from through-diffusion and half-cell technique. The design model parameters obtained from the two techniques were analyzed and compared with the batch sorption experiments.

Keywords: Through-diffusion, Half-cell, Clay, Salt diffusion

Introduction

For inhibiting the migration of the harmful contaminants to the surrounding groundwater compacted clay materials are used as landfill liners. Such a barrier limits the flow to such an extent where the contaminant migration is controlled [1]. Studies prove that the mechanism of flow through a fine-grained low permeable clay soil is governed by molecular diffusion [2, 3, 4, 5]. The clays used in liners have hydraulic conductivity as low as 10^{-9} cm/sec for which the advective flow is less significant. In such a case proper assessment of the effect of landfill wastes on the groundwater would require modelling of diffusive contaminant transport through the fine grained soil. Another important phenomenon controlling the contaminant transport is sorption which slows the contaminat transport and thereby delaying its presence in groundwater [6]. Laboratory diffusion testing enables the determination of the model parameters like the effective diffusion coefficient (D^*) and the adsorption coefficient or partition coefficient which gives a relationship between the solute sorbed to the mobile concentration in the solution [4, 6]. The estimation of the model parameters is very critical in assessing the migration rates of the contaminants through the barrier materials [7].

The present study is carried out to determine experimentally the model parameters which governs the diffusive flow of sodium through compacted bentonite soil which is used as barrier in landfills. Bentonite soil is often used as potential material for liners because of its high sorption capacity and low hydraulic conductivity. Two different laboratory methods has been conducted namely through-diffusion technique and half-cell technique. The salt solution used in this study is sodium chloride (Nacl). The maximum concentration of the salt used in both the experiments is 12000 ppm (0.2 M). The range is kept high keeping in view the large quantity of waste that gets dumped in the landfill over a large period. The compaction density is kept same in both the testing models which is 1.5g/cc. The purpose of conducting two

different laboratory methods to understand the migration rate of only one particular type of ion is done to have a comparative analysis of the model parameters which is not studied usually [8]. The paper also describes the batch test performed on soil and salt solution to obtain the adsorption coefficient. The sorption parameter so obtained can be used to compare with that obtained from laboratory diffusion tests.

A new application based software namely CONTRADIS is developed to obtain the model parameters from the experimental data. The software is developed to overcome the limitations of the semi-analytical commercially available software named POLLUTE. Previous studies used the concentration profile from the experimental data to best fit the theoretical data given by POLLUTE. But due to its high cost and inability of performing inverse analysis there is a need for a software program which can be easily available and provide with the model parameters. As CONTRADIS is used to get the model parameters from the inverse analysis of the obtained experimental data.

Diffusion Theory
Diffusion is a process in which a solute in a solution flow due to concentration gradient that is flow from a region of high concentration to low concentration. The diffusive flux usually follows Fick's first and second law [9]. The governing equation describing the transport of solute through saturated soil is given as [10, 11]:

$$\frac{\partial c}{\partial t} = \frac{D^*}{R_d}\frac{\partial^2 c}{\partial x^2}$$

(1)

where R_d is the retardation factor related with the sorption property of the soil.

Based on various initial and boundary conditions depending on the type of method used, analytical solutions to Eq. 1 have been developed for both through diffusion and half-cell method.

Materials and Methods
Soil used in the present study is a bentonite soil rich in montmorillonite mineral collected from a site in Rajasthan. The basic index properties of the soil is given in Table 1.

The contaminant considered in this study is Nacl solution which is prepared by dissolving 12g of Nacl in 1 liter of distilled water to make 0.2 molar Nacl. The concentration can be expressed as 12000 ppm.

The diffusion cell is made of Poly methyl methacrylate glass tubes also known by the trade name as Perspex glass. The material is used for its easy fabrication into required shape diffusion cell. Porous stones of 5mm thickness is used in both the experimental methods.

Table 1: Index properties of soil used

Property	Remarks
Dominant clay mineral	Montmorillonite
Liquid limit (%)	393
Shrinkage limit (%)	18.965
Specific gravity	2.76
Percentage of clay (%)	79.07
Specific surface area (m^2/g)	495

Through- Diffusion Technique:
In the double reservoir technique, the intact plug of barrier material (clay) is placed within the diffusion cell and compacted at a density of 1.5g/cc. A source and a collector reservoir is connected to the clay plug. A schematic diagram of the laboratory diffusion testing set-up is shown in Fig. 1. [11]. Initially the soil sample is saturated by putting distilled water in both the reservoirs. The saturation time for the soil sample is found to be 21 days and the saturated water content is 41.4%. Now after saturation the source reservoir is filled with the contaminant solution (here Nacl solution) and the collector reservoir solution is of pure distilled water. The initial concentration of the source solution is c_0. After the introduction of the leachate (here 0.2M Nacl) in the source reservoir, mass transport of the chemical constituents takes place by molecular diffusion due to concentration gradient. After suitable intervals the solution in both the reservoirs are collected and analysed for the sodium ion concentration by using flame photometer.
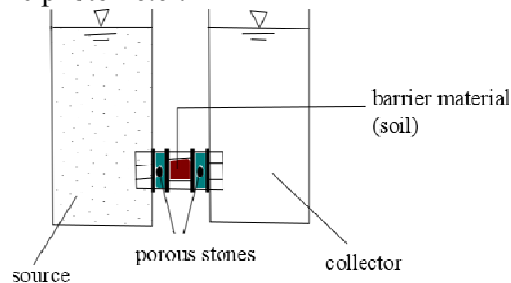

Fig 1: Transient through diffusion set-up

Using mathematical models, mass transport parameters are analyzed from the variation of the observed concentration profiles with time [12]. The initial and boundary conditions of the model as depicted is the same as available in the literature [1, 12]. Using the available initial and boundary conditions the analytical solutions to Eq. 1 showing the variation of concentration in the source and collector reservoir can be found elsewhere [12]. Values of D* and R$_d$, are determined from the inverse analysis by using the software CONTRADIS. The details of which is discussed in the later part of this paper.

Half-cell Technique

In order to determine the diffusion coefficient of the contaminants migrating through the barrier material, half-cell method can also be employed. The description of the method can be found elsewhere [13, 14]. In this method two half cells are filled with soil and compacted at the same density used for through diffusion testing (Fig. 2). Both the half cells are taken and saturated in water baths, one containing salt solution and distilled water in the other. In one of the half-cell the soil is contaminated, here saturated with 0.2M Nacl and in the other half-cell the soil is uncontaminated, saturated with distilled water. Now when both the half cells are connected together there will be migration of contaminants from one half-cell to the other. The contaminated half-cell from which the migration occurs can be termed as source and the other half cell can be termed as receiver. With time the concentration in the source cell decreases as the contaminants diffuses into the receiver cell. After the diffusion test which is terminated after 7 days, the soil mass in each half cell is sliced and analyzed for the variation of the concentration with depth. Both the half cells are of 3.9 cm diameter and the length of the samples maintained in each half cell is 4 cm
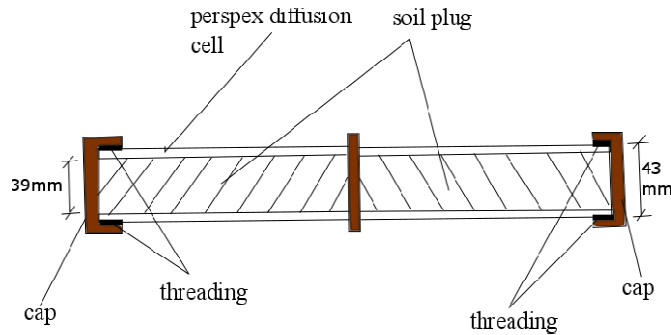

Fig 2: Half-cell set-up

The slices obtained were of 0.5 cm thickness and the weight of each slice is measured and and then it is mixed with 1 M ammonium acetate solution and mixed thoroughly in a rotary mixer for 24 hours. With proper mixing the mixture is transferred to a centrifuge tube and centrifuged for 5 minutes at 2000 rpm. After centrifuging the supernatant from each tube was analysed for the total sodium ion concentration in flame photometer. The solution was properly diluted by serial dilution process and then analysed for the sodium ion concentration. The soil settled at the bottom of the tube for each slice is collected carefully and oven dried to determine the amount of dry solids. Same amount of air-dried soil is analyzed for the adsorbed ion concentration by applying the same process as discussed. The mobile ion concentration will be the total concentration minus the adsorbed ion concentration. All together 16 samples are analysed for obtaining the relative concentration profile with distance.

In the infinite porous medium case the concentration profile does not reach the ends of the half-cell as depicted in Fig. 3a, where the origin is taken at the interface of the half cells. In the finite porous medium case the concentration profile reaches to the ends of the half-cell as depicted in Fig. 3b. Corresponding to the initial and boundary conditions [13], the solution to Eq. 3 for both infinite and finite cases is stated nicely in the available literature [13, 14].
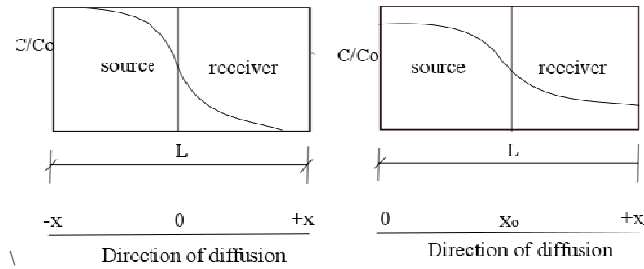
Fig 3a: Infinite case   Fig 3b: Finite case

Codes are formulated for both the forward and inverse analysis of the solutions using a coding language VISUAL BASIC which is then used for the development of CONTRADIS software based on .NET framework. The CONTRADIS application takes the experimental data and runs the forward as well as inverse analysis to give the model parameters.

Batch Test:

Batch equilibrium test is performed on air-dried soil to determine the sorption characteristics of the clay soil with respect to sodium ions. The soil to solution ratio maintained in the test is 1:20. Maximum soil to solution ration that can be taken is 1:4 [11]. 10 grams of the soil is mixed with 200 ml of Nacl of different initial concentrations. Six different initial concentrations are maintained in six different soil samples having weight of 10 grams. The soil solution is mixed thoroughly in an orbital shaker for 48 hours. After thorough mixing the slurries are taken in a centrifuge tube and centrifuged for 2000 rpm for 10 minutes. The supernatant from each tube is analysed for the equilibrium concentration of the sodium ion by flame photometer. The results are plotted to determine the adsorption isotherm which relates the sorbed ion concentration q with the equilibrium ion concentration C_e. The sorbed ion concentration is determined as:

where V is the volume of the solution and   is the mass of the soil sample (here 10 grams).

CONTRADIS:

The name CONTRADIS stands for "**CON**taminant **TRA**nsport due to **DI**ffusion in **S**oils". PULLUTE is the only one software package available that is widely used by Geo-environmental engineers for contaminant migration analysis. It is being used in the industry since fifteen years. But the drawbacks of this software include non-availability of option for inverse analysis capabilities and high cost, due to which everyone cannot use it. This software is being built for overcoming the limitations of POLLUTE.

    The software package is based on the .NET framework by Microsoft and can run in Windows operating systems, i.e., Windows 8 and later. The software can perform inverse analysis to estimate the diffusion and linear sorption parameters of soils such by comparing the experimentally measured and theoretically computed concentration data by minimizing the RMSE (root mean square error). The technique used for inverse analysis is Particle Swarm Optimization (PSO) [11]. The software is verified on the synthetic data obtained from calculated concentration values as an input data taken from previous available literature.

Results and Discussions

Results from through-diffusion technique

The concentration profile is obtained after the proper analysis of the concentration of sodium ion from the source and collector reservoir. The concentration data is collected for 60 days and the relative concentration is calculated by dividing the obtained concentration by the initial concentration. The concentration profile is shown in Fig. 4 (a). It is observed that the concentration in the source reservoir decreases with time and concentration in the collector reservoir increases with time. The collector reservoir shows constant concentration for few days and then it starts increasing. This is because of the sorption of the sodium ion by the clay soil. The experimental data is used in CONTRADIS for the inverse analysis which compares with the theoretical obtained data by minimizing the RMSE error. The model parameters obtained from the software by inverse analysis is given in Fig. 4(b). The effective diffusion coefficient so obtained is $3.3 \times 10^{-10} m^2/sec$ and retardation factor is 10.
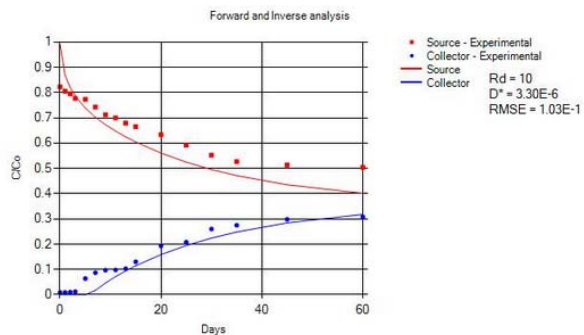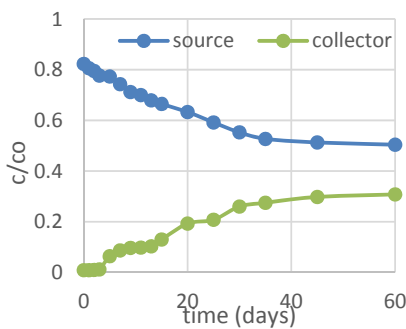
Fig 4 (a): Conc. profile for through diffusion   Fig 4 (b) CONTRADIS conc. profile

Results from Half-Cell Technique

After the diffusion testing is over in half-cell method the soil is extruded into 0.5cm slices from both the halves. Each slice is weighed and then analysed for sodium ion concentration. The mobile ion concentrations are determined after subtracting the adsorbed ion concentration from the total sodium ion concentration. The concentration profile is shown in Fig. 5 (a). The experimental data is analysed in CONTRADIS for getting the model parameters by inverse analysis. The best fit curve showing the theoretical concentration data and experimental data is shown in Fig. 5 (b). The effective diffusion coefficient so obtained is $1.51 \times 10^{-9} m^2/sec$ and retardation factor is 1.5. It is seen that the theoretical curve obtained from CONTRADIS does not fit properly in both the testing models. This can be attributed to the fact that the governing equation assumes the sorption to be linear but than in reality the sorption is usually non-linear for a wide range of ions.
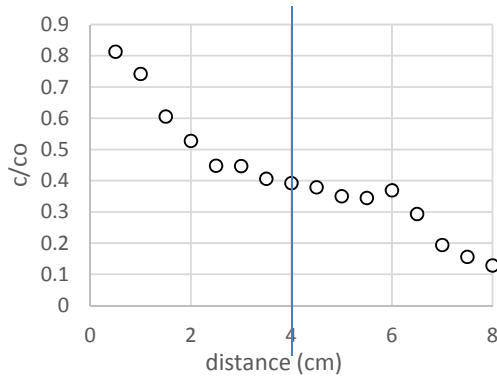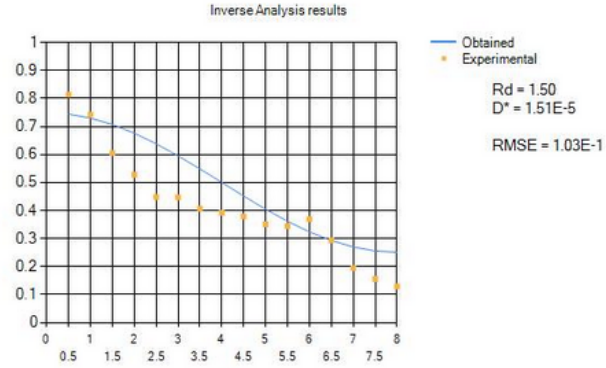
Fig 5 (a): Conc. profile for Half-Cell   Fig 5 (b) CONTRADIS Conc. Profile

The variation in the model parameters is because of the mechanism involved in both the methods. The mechanism of contaminant migration in through-diffusion technique is based on the contaminant transport through a soil plug, but in half-cell method it is spatial migration of contaminant within the soil mass. Proper analysis has to be carried out for both the type of methods for different type of ions to understand the sorption mechanism that alters the diffusion coefficient values for both the methods.

Results from Batch Equilibrium Test:
Batch test results are plotted and the adsorption isotherm is obtained. The isotherm if made linear does not give the best fit whereas the Freudlich isotherm fits more accurately. The equations describing the process to determine the retardation factor from linear and Freudlich model can be found elsewhere [10]. The retardation factor from the linear model obtained experimentally is 4.8 and the retardation factor obtained from the linearized Freudlich model is 6.1. Based on the laboratory batch test the retardation factor so obtained is seemingly close to through diffusion testing which is 10. The retardation coefficient obtained from half-cell technique is less. This can be attributed to the experimental error which might occur in saturating both the half cells at the same time and also proper contact between the cells might not be possible always.

Summary and Conclusion
Two different types of experimental techniques are employed to estimate model parameters, viz; through diffusion technique and half-cell technique. The experimental data obtained from both the methods are used in the newly developed CONTRADIS software to obtain the theoretical curve with minimum RMSE error. The model parameters are obtained by inverse analysis of the experimental data. The effective diffusion coefficient values and retardation factors obtained from both the methods are not similar. This is due to the fact that the mechanism of diffusive transport is not similar. In order to verify the adsorption parameters batch test is performed on the same soil and the adsorption isotherm is obtained more accurately by fitting Freudlich isotherm. The retardation factor so obtained is almost near to the through diffusion result. So the diffusion coefficient and retardation factor obtained from through diffusion technique can be said to be more realistic. Unfavorable results in half-cell technique may occur because of improper contact between the half cells and also saturating both the cells at the same time one with contaminant and the other with pure water might not

be practical all the time. So a wide range of study for various types of ions is necessary to analyze the model parameters obtained from both the methods.

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