Effect of Inorganic Salt Solutions on the Hydraulic Conductivity and Diffusion Characteristics of Compacted Clay

Partha Das and T. V. Bharat

Abstract Clayey soils rich in montmorillonite content are increasingly used as liner material for various landfill facilities because of their very low saturated hydraulic conductivity, high sorption potential and better self-sealing capacity. However, the performance assessment of such a facility requires long-term hydraulic conductivity and diffusion studies of the clayey soil under the influence of different pore fluids. In this paper, an extensive study was carried out to understand the effect of various inorganic salt solutions such as lithium chloride, sodium chloride and potassium chloride on the montmorillonite rich bentonite clay by performing long-term hydraulic conductivity tests and transient through-diffusion tests. A software package named CONTRADIS was utilized in the present study which was able to perform inverse analysis for estimating the diffusion parameters from the experimental data. The experimental study suggests that the electrolyte concentration changes the hydraulic conductivity and diffusion coefficient significantly. The hydrated cationic radius also has considerable effect on the equilibrium hydraulic conductivity of the soil.

Keywords Through-diffusion · Long-term hydraulic conductivity · CONTRADIS

1 Introduction

For restricting the migration of the contaminants to the surrounding environment, bentonite soils are used as potential barrier material. Bentonites barriers are expected to have saturated hydraulic conductivity less than 10^{-9} m/s throughout the life of a landfill for effectively reducing the contaminant flow through them. However, the hydraulic conductivity of such barrier materials was found to increase significantly when permeated with inorganic salt solutions (Lee and Shackelford 2005). The hydraulic conductivity of fine grained soils like bentonites is greatly influenced by the minerals present in the soil, the composition of exchangeable cations and the cations present in the pore fluid (Rao and Mathew 1995). Hence, a study on long-term

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effect on the clay barriers under the influence of different inorganic salt solutions becomes very important (Shackelford et al. 2000; Kolstad et al. 2004).

Also, flow through fine grained soils is mostly governed by the diffusion mechanism, as the hydraulic conductivity is low due to which the advective transport is negligible (Bouazza and Van Impe 1997; Shackelford et al. 1989). In such a condition, the estimation of the model parameters like the effective diffusion coefficient and retardation factors becomes very essential for the design of the liner facilities. Various laboratory techniques are adopted to estimate the model parameter (Barone et al. 1992; Shackelford and Daniel 1991; Van Loon and Jakob 2005; Robin et al. 1987). Amongst all the technique, through-diffusion technique is mostly preferred as is it a non-destructive testing methodology (Bharat 2009). The laboratory estimated diffusion coefficient was found to vary considerably when salt solutions were allowed to diffuse through compacted soil over a longer period of time (Das and Bharat 2017). The influence of the size of the cations and the valence of the cations was also found to be significant. Most of the previous studies were concerned with the size and valence effect cations present in the pore fluid; however, an extensive study on the influencing factors on both hydraulic and mass transport parameter, when permeated with varied electrolyte solutions, remains to be completed.

In this paper, a detailed experimental study on the influence of different pore fluids having a wide range of concentrations on the compacted bentonite soil was presented. Long-term hydraulic conductivity tests were conducted using falling head technique by permeating the compacted bentonite soil with different salt solutions like lithium chloride, sodium chloride and potassium chloride. Also, through-diffusion tests were conducted to understand the variation in the mass transport parameters for the pore fluids in which the hydraulic conductivity variation was significant. A Java-based application package named CONTRADIS was utilized to obtain the model parameters from the experimental concentration profiles, by performing inverse analysis (Das et al. 2016).

2 Materials and Methods

In the present work, bentonite soil procured from Barmer district in Rajasthan was used. The index and surface properties of the studied bentonite are given in Table 1.

2.1 Long-Term Hydraulic Conductivity Tests

Air dried soil sample was compacted in a hydraulic conductivity cell fabricated from acrylic solid tube. The internal diameter of the cell was 2.4 cm, and the thickness was kept to be 1 cm. The soil was statically compacted at a bulk density of 1.4 g/cc. After compaction, the soil sample was rigidly held between two porous stones on either end by fixing the caps supported by threading on the outer side of the cell.

Table 1 Index and surface properties of the studied bentonite (Bharat and Das 2017)

Property	Value
Liquid limit	393
Plastic limit	50
Shrinkage limit	18
Specific gravity	2.77
Montmorillonite content (%)	55
Specific surface area (m^2/g)	495
Cation exchange capacity (meq/100 g)	71.7

Hydraulic conductivity tests were conducted by falling head technique in accordance with ASTM D5856. A head of 8.75 m was provided to saturate the soil sample, and saturation was ensured when the fall in head became steady. Saturation was also cross checked by monitoring the weight of the soil sample with time, a constant weight of the soil sample when achieved indicated complete saturation. Hydraulic conductivity tests were commenced after saturation was completed, by permeating the soil sample with different salt solutions having different concentrations. Care was taken to remove the distilled water after saturation process and then filling of the burettes with the pore fluid of required concentrations. The fall in head was regularly monitored until equilibrium hydraulic conductivity was reached.

The test was terminated when the hydraulic conductivity values become constant over a period of 3–4 days. Three series of hydraulic conductivity tests using different electrolytes were conducted to ascertain the dependency of equilibrium hydraulic conductivity on the size of ions and electrolyte concentration. The series consisted of 0.01, 0.1, 0.5 and 1 molar aqueous solutions of lithium chloride (LiCl), sodium chloride (NaCl) and potassium chloride (KCl). All the electrolytes were analytical/laboratory grade, procured either from Merck (Germany) or Spectrochem (India) and supplied by a local vendor. The tests were not conducted for concentration less than 0.01 M as any concentration below this does not influence the exchange process and the exchangeable cations on the surface dominate the clay behavior (Rao and Mathew 1995).

The hydraulic conductivity test result showed that the equilibrium Ks value increased more than the limiting value when the soil sample was permeated with KCl solutions even at lower concentrations. Hence, diffusion tests were conducted with only KCl solution as the pore fluid.

2.2 Laboratory Through-Diffusion Test

Through-diffusion test setups were also fabricated from acrylic tubes having internal diameter 2.4 and 1 cm thickness. The air dried soil sample was compacted statically at the same density as was maintained for the long-term hydraulic conductivity

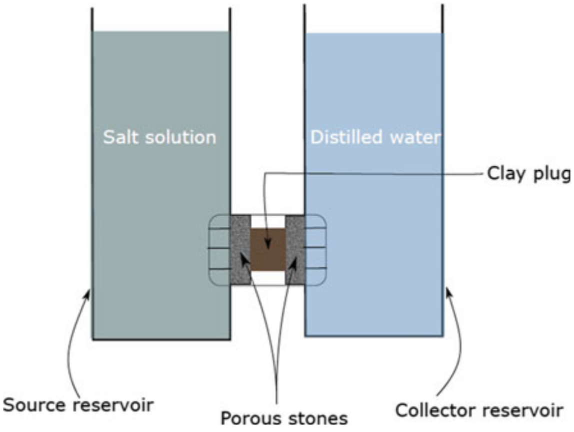

Fig. 1 Illustration of laboratory through-diffusion setup

tests. The diffusion cell was connected on either ends to two reservoirs (source and collector) as shown in Fig. 1. Both the reservoirs were then filled with distilled water to saturate the soil sample. After saturation was ensured by constant weight method as explained earlier, diffusion tests were commenced. The solution in the source reservoir was replaced with salt solution of known concentration, and the water in the collector reservoir was removed and filled with fresh distilled water. During the diffusion process, the solution in both the reservoirs was stirred to avoid deposition of any salts at the bottom. At frequent interval of time, samples were collected from both the reservoirs and analyzed for concentration using flame photometer. Diffusion tests were conducted using KCl solution as the pore fluid having same concentration range that was used in the hydraulic conductivity tests.

3 Theoretical Background for Diffusion

The governing differential equation that describes the transport of chemical species through saturated soil is given as

$$\frac{\partial c}{\partial t} = \frac{D_e}{R_d}\frac{\partial^2 c}{\partial x^2} \tag{1}$$

where c is the salt concentration, t is the time of diffusion, D_e is the effective diffusion coefficient, x is the distance along the length of the soil sample, and R_d is the retardation factor which describes the sorption potential of a soil. The retardation factor for linear sorption case is given as

$$R_d = 1 + \frac{\rho K_d}{n} \tag{2}$$

where K_d is the distribution coefficient, ρ is the dry bulk density and n is the porosity of the clay plug. Equation 3 gives the initial condition, and the boundary conditions of the diffusion experiment are given by Eqs. 4 and 5 (Rowe and Booker 1985):

$$c(0 < x < L, t = 0) = 0 \tag{3}$$

$$c(x = 0, t) = c_0 + \frac{nD_e}{H_s} \int\limits_0^t \left(\frac{\partial c}{\partial x}\right)_{x=0} \mathrm{d}t \tag{4}$$

$$c(x = L, t) = -\frac{nD_e}{H_c} \int\limits_0^t \left(\frac{\partial c}{\partial x}\right)_{x=L} \mathrm{d}t \tag{5}$$

Equation 4 describes the boundary condition at the source reservoir, and Eq. 5 describes the boundary condition at the collector reservoir. Here, c_0 is the initial concentration of the contaminant species at time $t = 0$; H_s and H_c are the equivalent heights of source and collector reservoirs, respectively.

The analytical solution to the governing differential equation (not shown here) considering the above initial and boundary conditions was given by Bharat (2013) using Laplace transformation. This analytical solution was utilized to estimate the model parameters which are the effective diffusion coefficient and retardation factor by inverse problem. The inverse problem was solved by minimizing the error between the experimental concentration profile and the theoretical data. The minimization was performed by using particle swarm optimization technique (Bharat et al. 2012). A Java-based application suite was developed to perform such inverse analysis problem. The relative concentration profiles obtained experimentally were given as input in the software package along with the density and equivalent heights of the reservoir. The software was then capable of estimating the optimized value of the model parameters from the input data.

4 Results and Discussions

4.1 Long-Term Hydraulic Conductivity Test Results

The variation of the equilibrium hydraulic conductivity with time for all the salt solutions at different concentrations was shown (Figs. 2, 3 and 4). It can be observed from the figures that the hydraulic conductivity increases with time for all the concentration, maximum being observed for a concentration of 1 M. This behavior is governed by the diffused double layer thickness (DDL). As the concentration of a particular pore fluid increases, the inter-particle attractive force increases between the clay platelets, and as a result, the DDL thickness is suppressed. With the supression of the

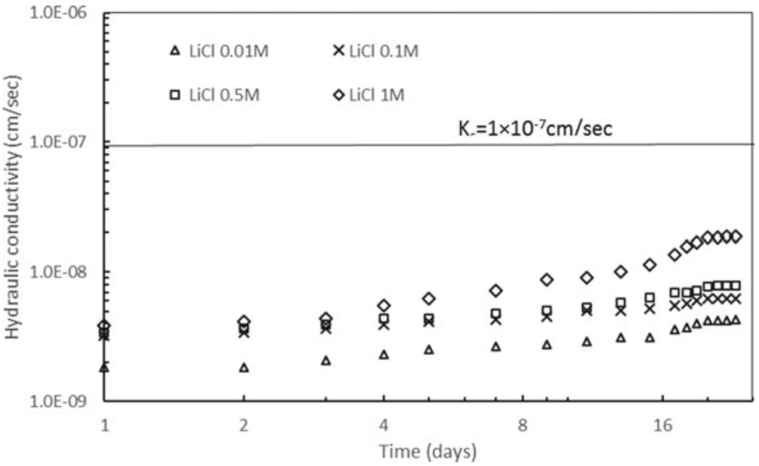

Fig. 2 Temporal variation of hydraulic conductivity of the bentonite with LiCl as the permeant fluid

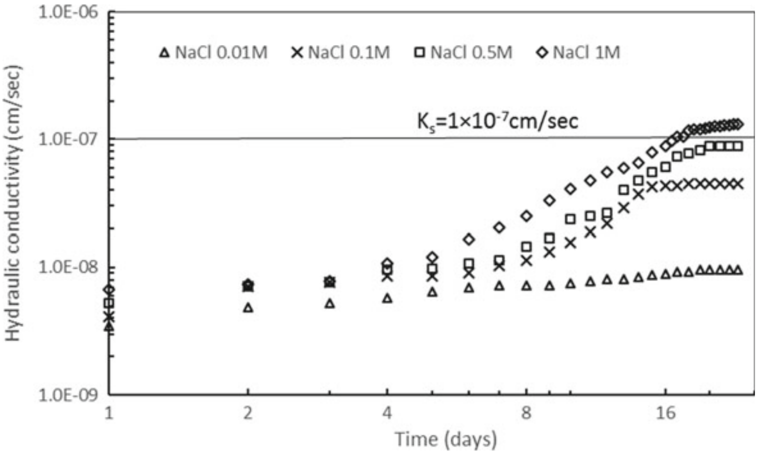

Fig. 3 Temporal variation of hydraulic conductivity of the bentonite with NaCl as the permeant fluid

DDL thickness, inter-particle forces increases which leads to the formation of flocculated structure which in turn results in significant increase of *Ks*. The equilibrium hydraulic conductivity of the soil exposed to LiCl of 0.01 M was 4.27×10^{-9} cm/s, whereas for the same soil, when exposed to LiCl solution of 1 M concentration, the equilibrium hydraulic conductivity increases to 1.88×10^{-8} cm/s, an increase of 4.4 times. Another important aspect that can be brought out from Figs. 2, 3 and 4 is that at 0.01 M concentration, the equilibrium hydraulic conductivity in the presence of Li^+ and Na^+ is of the same order; however, the conductivity changes by at least

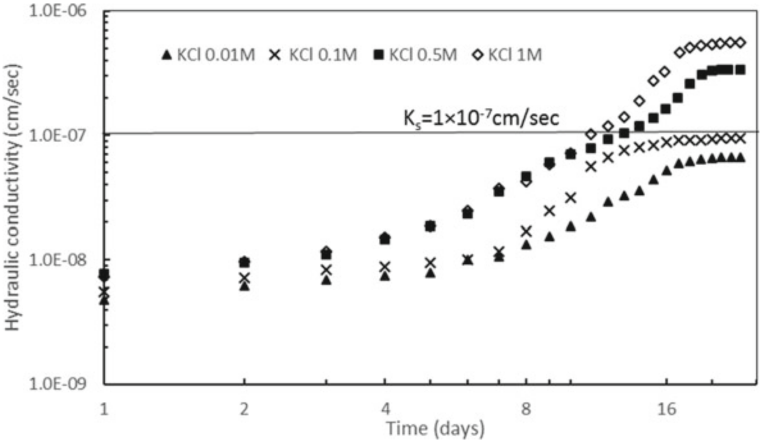

Fig. 4 Temporal variation of hydraulic conductivity of the bentonite with KCl as the permeant fluid

one order of magnitude at a concentration of 1 M. This can be attributed to the fact that at higher concentrations, more exchangeable cations are present which are able to replace the cations in the clay surface, and thus, it compresses the DDL layer reflecting an increase in the equilibrium hydraulic conductivity.

With Li^+ as the diffusing ion, even at higher concentration of 1 M, the limiting value of hydraulic conductivity for liners is not crossed. However, at higher concentration for both sodium and potassium ions, when present in the pore fluid, the limiting value is exceeded. The hydrated cationic radius of K^+ and Na^+ being less than Li^+ ion, the hydraulic conductivity increase is very significant as the DDL is suppressed more compared to the lithium ion providing more flow path for the fluid to migrate and attain higher equilibrium hydraulic conductivity. This particular behavior is not properly understood by the Gouy–Chapman theory, which considers the ions to be point charge and the influence of the size of the cations is neglected. It is, however, qualitatively understood that any decrease in the hydrated ionic radius of the same valence suppresses the double layer thickness (Rao and Mathew 1995).

The influence of the hydrated cationic radius on the equilibrium hydraulic conductivity is shown in Fig. 5. It can be concluded from this figure that with the decrease in the cationic radius of the exchangeable ions, the equilibrium hydraulic conductivity increases. The increase was significant at a concentration of 1 M where the equilibrium hydraulic conductivity in the presence of Li^+ ion was 1.88×10^{-8} cm/s, and in the presence of K^+ ion, it was observed to be 5.58×10^{-7} cm/s, an increase of almost 29 times.

The lowest increase, however, was observed for a concentration of 0.01 M. So for an increase in concentration leads to an increase in the hydraulic conductivity in the presence of all the three salt solutions, and also, any decrease in the cationic radius causes increase in the hydraulic conductivity. This is due to the suppression of the DDL thickness in both the cases which in turn increases the effective void size that

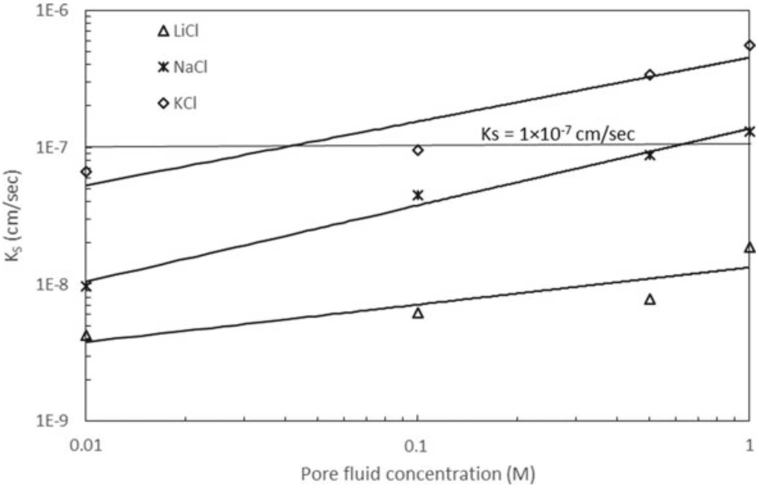

Fig. 5 Variation of equilibrium conductivity of the bentonite with salt concentration for different salts

is changed from micropores to macropores (Rao and Mathew 1995) for which there is a significant increase in the equilibrium hydraulic conductivity. The increase in cationic sizes, therefore, is favorable to the performance of the landfill liner.

4.2 Through-Diffusion Test Results

More detrimental consequences were observed in terms of equilibrium hydraulic conductivity, when KCl was present in the pore fluid. Under such a condition, it becomes very important to understand the migration rate of potassium ions corresponding to different concentrations. Hence, diffusion tests were conducted only with KCl as the diffusing chemical species having the same concentration range as was used in the hydraulic conductivity tests. The experimental concentration profiles for both source and collector reservoirs, with time for compacted soil subjected to KCl solutions of different concentration, are shown in Fig. 6. The effect of concentration can be qualitatively understood from this figure. It can be seen here that when the concentration of KCl solution was 0.01 M, the relative concentration of the source reservoir was around 0.65 after a period of two months. However, at 1 M KCl solution, the relative concentration reached 0.5, indicating a very fast migration rate at this concentration. This is in coherence with what was observed from the hydraulic conductivity test results.

In order to quantitatively understand the influence of different concentrations of KCl electrolyte solutions, experimental plots were utilized to obtain the model parameters which are the effective diffusion coefficient and the retardation factors.

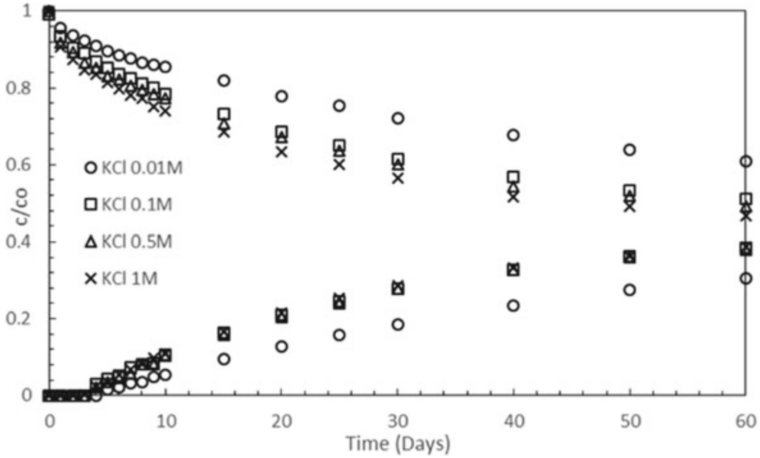

Fig. 6 Temporal data of measured salt concentration in source and collector reservoirs for KCl

The Java application CONTRADIS uses the analytical solution of the governing differential diffusion equation to obtain the inverse analysis (theoretical) plots for an optimized value of the model parameters. Figures 7, 8, 9 and 10 give a comparison of the experimental concentration profile with the theoretical results. It is observed that the theoretical data fits very well with the experimental results.

The effective diffusion coefficient, D_e, in the case of potassium ion (K^+) is found to have increased with the increase in concentration (Figs. 7, 8, 9 and 10). At a concentration of 1 M, the effective diffusion coefficient increases to one order of magnitude (Fig. 10) compared to the case when the concentration was 0.01 M (Fig. 7). The

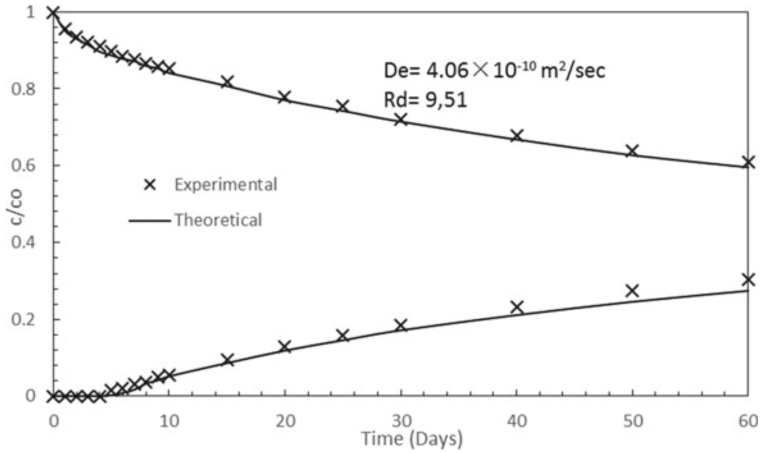

Fig. 7 Comparison of the experimental concentration profile with the theoretical data for 0.01 M KCl

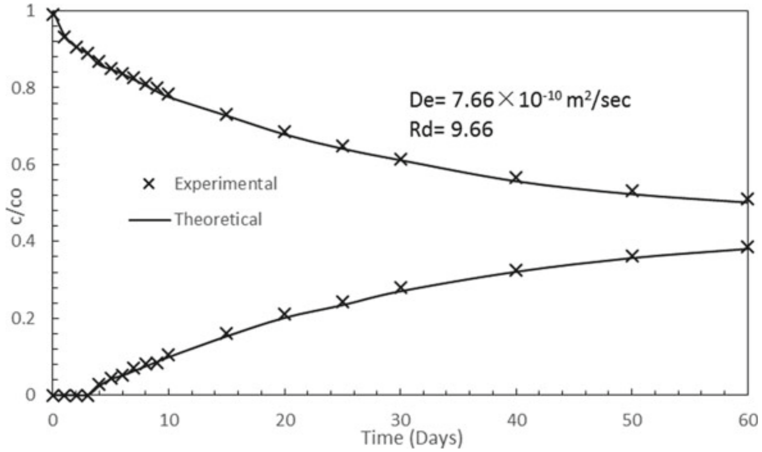

Fig. 8 Comparison of the experimental concentration profile with the theoretical data for 0.1 M KCl

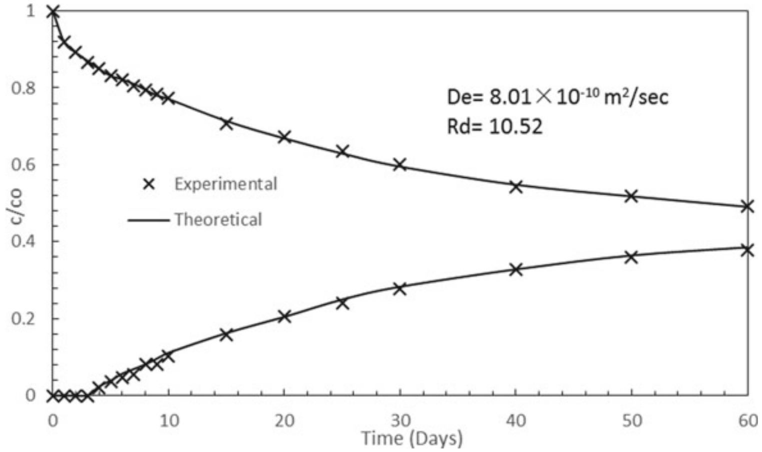

Fig. 9 Comparison of the experimental concentration profile with the theoretical data for 0.5 M KCl

reason behind this is that with increase in concentration more number of potassium ions is present in the bulk solution that replaces the exchangeable cations present in the mineral surfaces. As a result, the DDL thickness gets reduced which in turn allows a free flow path for the ion to move.

The retardation factor, which relates to the sorption potential of the soil, is found to increase with the increase in concentration. This is attributed to the fact that at higher concentrations, more number of potassium ions which are present in the bulk solutions are sorbed onto the mineral surfaces to effectively satisfy the charge density. Table 2 shows the comparison of hydraulic conductivity and diffusion coefficient of

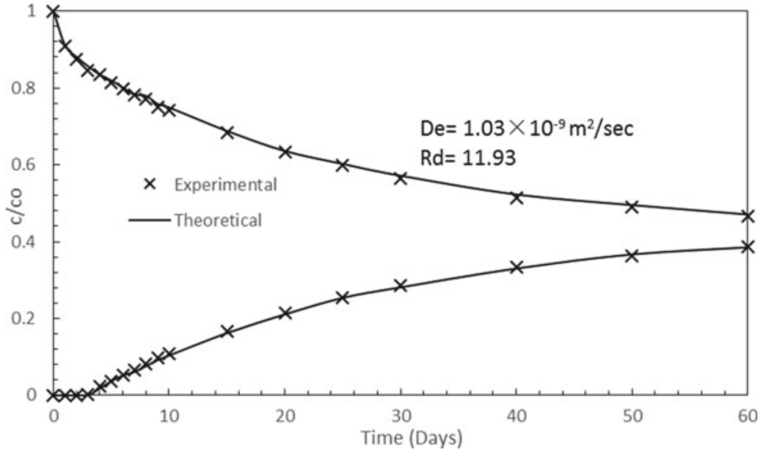

Fig. 10 Comparison of the experimental concentration profile with the theoretical data for 1 M KCl

Table 2 Comparison of hydraulic conductivity and diffusion coefficient with KCl as pore fluid

Salt used	Conc. (M)	Keq (m/s)	D_e (m^2/s)
KCl	0.01	6.69×10^{-10}	4.06×10^{-10}
	0.1	9.48×10^{-10}	7.66×10^{-10}
	0.5	3.38×10^{-9}	8.01×10^{-10}
	1	5.60×10^{-9}	1.03×10^{-9}

soil when it is permeated with KCl solution of varied concentrations. As discussed earlier when the concentration of the pore fluid increases, it leads to the suppression of the DDL thickness resulting in the formation of a pervious flocculated structure. As a result, there is a significant increase in the equilibrium hydraulic conductivity. The effective diffusion coefficient also increases considerably at this stage as the mobility of the ion through the soil pores increases.

5 Summary and Conclusions

Long-term hydraulic conductivity tests were conducted by permeating a saturated soil with different salt solutions having a wide range of concentrations. The cations present in the salt solutions are found to have significant impact on the equilibrium hydraulic conductivity values. The hydraulic conductivity increases with the increase in the pore fluid due to the suppression of the DDL thickness. The limiting value of the hydraulic conductivity for liner design was crossed when sodium ions are present in the pore fluids at concentrations greater than 0.5 M. When potassium ions are present in the pore, the limiting value is exceeded even at a lower concentration of 0.1 M.

The size of the diffusing ion also plays a significant role in changing the equilibrium hydraulic conductivity value. The hydrated cationic radius of lithium ion being large compared to sodium and potassium ion, the migration rate is found to be significantly low when lithium is present in the pore fluid. Bigger size cations like lithium is found to have hydraulic conductivity value much lesser than the limiting value for liner design and as such they do not pose any threat to the liners in the long run.

Laboratory through-diffusion tests were conducted only for KCl as the diffusing chemical species. Only KCl solution was selected for diffusion testing because even at lower concentrations potassium ions were able to exceed the limiting value of hydraulic conductivity for the liner design, and hence, it had more detrimental impact compared to the other pore fluids. It was observed that the migration rate of the potassium ions increased rapidly as the concentration was increased. This was reflected by the effective diffusion coefficient value that was obtained by inverse analysis through CONTRADIS. The effective diffusion coefficient, when potassium was present in the electrolyte solution, increased to one order of magnitude when the concentration increased to 1 M. Both equilibrium hydraulic conductivity and effective diffusion coefficient increased with concentration of KCl, due to the presence of small DDL thickness all around the clay platelets resulting in free flow paths for the ions to diffuse.

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