

Effect of Counter Ions on the Diffusion Characteristics of a Compacted Bentonite

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Abstract Salt diffusion studies through compacted bentonites are important for designing the waste disposal facilities and assessment of the existing facilities. As the behavior of plastic clays is governed by the physical chemistry of the clay surface–electrolyte interactions, the effect of physicochemical parameters on diffusion rates of the bentonites is required to be studied. In this paper, transient through diffusion tests were conducted with different salts that contain different monovalent cations and a divalent cation. The influence of hydrated size and valence of the cations on the contaminant migration was studied experimentally. A Java based inverse analysis suit, CON-TRADIS, was utilized for estimating the mass transport parameters from the experimental observations. The effect of hydrated size and valence of the cations on the mass transport parameters of the bentonite was qualitatively analyzed using diffuse double layer theory. The diffusion coefficient was found to vary about one order magnitude with the hydrated size of the cation. The significance of the variation in mass transport parameters was analyzed using the simulated concentration profiles along the depth of the clay liner.

Keywords Diffusion coefficient · Cation size · Bentonite · Through-Diffusion · Contaminant Migration

Introduction

Landfills are the unparalleled engineered containment facilities for addressing the ever-growing waste disposable problems. The generated leachate from the disposed waste, in these facilities, is encapsulated with bentonite liners to reduce exposure to the surrounding environment. The quality of the bentonite is important for specific application. The engineering parameters such as hydraulic conductivity, retention capacity for cations, and self-sealing ability [6, 9, 16, 19, 26, 53] vary with the quality of the bentonite. Higher quality bentonites [32], that are highly plastic in nature, are also used in hazardous toxic waste containment facilities [20, 45] and high level nuclear waste repositories as buffer and backfill materials [24, 38, 56, 57]. Diffusion is the dominant transport mechanism for contaminant migration through compacted bentonites due to the low hydraulic conductivity [17, 49]. The advection transport is, therefore, absent in these facilities as the barriers are nearly impermeable to the migration of salts under the hydraulic gradients. The diffusion and retardation characteristics of the compacted bentonites for different salts and different initial compaction densities are important for the design of these facilities. Several laboratory diffusion studies are used to estimate the design parameters. Laboratory techniques such as through-diffusion [3, 4, 30, 41, 42], in-diffusion [33, 47–49], out-diffusion [44, 54], and half-cell techniques [28, 40] are routinely used to estimate the temporal and spatial changes of contaminant concentration. Transient through-diffusion (TTD) technique is more expedient due to non-destructive nature and simplicity in the experimental measurements, although all the methods lead to the same design parameters [7, 8]. The measured concentration data is analyzed using mathematical formulation based on Fick's diffusion equation [46]. Finite mass boundary conditions are

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employed in the mathematical model to represent the boundary conditions in through-diffusion technique [41]. Several past studies developed numerical and semi-analytical solutions to the TTD problem by assuming the validity of linear sorption mechanism [14, 15, 26, 29, 36, 42]. A closed-form analytical solution was developed for TTD problem by Bharat [9] which is computationally robust. The model parameters are accurately estimated using optimization techniques that minimize the error between the measured and theoretically obtained concentration data [14]. The focus of the existing diffusion studies using compacted clays are only on the improvement of experimental methodology, accuracy of the solution to the mathematical model, or accuracy of the model parameter estimation. However, the influence of physicochemical factors on the diffusion characteristics of plastic clays remains to be completed.

The mineral surfaces, in expansive clays, carry net negative charge due to isomorphous substitution. A diffuse double layer (DDL) is formed around the platelets in the presence of electrolytes [34]. The surface properties such as specific surface area and cation exchange capacity influence the formation of the DDLs. The thickness of the DDL controls the engineering behavior of expansive clays. Several interrelationships between surface properties; index and engineering properties are, therefore, available [22, 31, 37]. The DDL thickness changes with the change in electrolyte concentration; cation properties; dielectric constant; and cation complexion between the surface cations and the cations in the pore-fluid [10–12, 34, 39, 51]. The cation complexion is an important factor in diffusion studies due to the fact that the salt diffusion is a slow process and sufficient time is available for exchange of surface cations with the cations present in the pore-fluid. The changes in the DDL thickness may influence the mass transport parameters, therefore. The effectiveness of the bentonite is found to be deteriorating with long-term exposure to the salts in the long-term hydraulic conductivity experiments with varying salt concentrations and counter ions [16, 27, 32]. However, the influence of cation characteristics on the mass transport parameters is not available.

In this paper, laboratory through-diffusion studies were conducted with different salts. The influence of cation valence and hydrated cation radius was studied on the mass transport parameters. The influence of hydrated cation radius on the diffusion coefficient was found to be highly significant.

Materials and Methods

A high quality bentonite procured from Barmer district of Rajasthan, India, was used for diffusion studies in this work. This plastic clay is considered to be the most suitable liner material for upcoming landfills and buffer

material for future nuclear waste repositories in India. The index and surface properties of the bentonite are studied recently by Gapak et al. [23] that were reproduced in Table 1. Hydraulic conductivity of the compacted bentonite was conducted using falling head technique in accordance with ASTM D5856 [2]. A higher hydraulic gradient was, however, used for reducing the test duration due to very low hydraulic conductivity [50]. The air-dried soil sample was statically compacted into a permpex cell of 2.4 cm diameter and 1 cm height to an initial bulk density of 1.5 g/cm^3 . The end caps were fixed to restrict the volume change during hydration, similar to rigid wall permeameter. A head of 6.4 m was applied for saturation. The permeability cell was frequently weighted to obtain an equilibrium value. The estimated hydraulic conductivity values from the repeated tests were also verified to ensure full saturation of the compacted clay. The hydraulic conductivity of the studied bentonite was $6.9 \times 10^{-12} \text{ m/s}$.

Laboratory Diffusion Testing

Through-diffusion testing was used, in this study, as this technique is non-destructive and the concentration profile along the soil depth is not required. The testing is faster, further, as the sample dimension does not influence the accuracy of model parameter estimation [46]. One centimeter thickness and 2.4 cm diameter clay plugs were, therefore, used in this study. The diffusion cell was fabricated from a solid plexiglass tubes to accommodate the clay plug and 5 mm thick porous stones as shown in Fig. 1a. A detailed photograph of the through-diffusion setup and the drawing for diffusion cell were provided in Fig. 1a, b. The clay sample in air-dry state was statically compacted to 1.5 g/cm^3 in diffusion cells and the porous discs were placed on either side of the clay plug. The cell was then attached to the reservoirs on either side by capping on the outer thread of the cell. A rubber gasket was used around the outer threading to prevent leakage. The reservoirs were then filled with distilled water for the saturation from both sides. The saturation took nearly 30 days which was assessed by weighing the diffusion cell at regular intervals. The saturated water content under no-volume change conditions was found to be $\sim 45\%$. The diffusion experiment was commenced soon after the saturation of the plug by replacing the source reservoir with known salt concentration. The water in the collector reservoir was also replaced with distilled water to avoid the influence of any excess salt deposition from the clay plug on diffusion. The electrolytes in the reservoirs were regularly stirred to maintain the uniform concentration through the reservoir at any given time. A 10 ml samples were collected from the reservoirs at frequent intervals of time for determining the concentration. Concentration of a given

Table 1 Index and surface properties of the studied bentonite

| Property | Value |
|---|--------------------------|
| Liquid limit (%) | 393 |
| Plastic limit (%) | 50 |
| Shrinkage limit (%) | 18 |
| Specific gravity | 2.77 |
| Clay size (%) | 78 |
| Specific surface area (m ² /g) | 495 |
| Cation exchange capacity (meq/100 g) | 71.7 |
| Montmorillonite content (%) | 55 |
| Hydraulic conductivity (m/s) | 6.89 × 10 ⁻¹² |

cation was measured using flame photometer (®Systronics India, Type-128) after required dilution. The measured concentration with time in both source and collector reservoirs were used for the diffusion analysis. Different salts with varying cation valence and cationic radius were considered for diffusion studies. The salt characteristics were presented in Table 2. An initial salt concentration of 0.2 M was used in the source reservoir in all the diffusion tests.

Theoretical Background

The salt diffusion through clays is studied using Fick’s diffusion equations. One-dimensional governing diffusion equation for saturated soils is given by

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

where c is the salt concentration in the soil pores, t is the diffusing time, D_e is the effective diffusion coefficient, n is the porosity, x is the distance from the source, and R_d is the retardation factor which describes the sorption potential of a soil. The retardation factor for linear sorption case is expressed 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. The initial condition of the diffusion experiment was given by

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

where L is the length of the clay plug. The initial condition reflects that the clay is free of contaminant at the beginning of the experiment, $t = 0$. The boundary conditions at the source and collector reservoirs, respectively, are given by

Rowe and Booker [41], Barone et al. [4], Rowe et al. [42], Bharat [8], Bharat et al. [15].

$$c(x = 0, t) = c_0 + \frac{nD_e}{H_s} \int_0^t \left(\frac{\partial c}{\partial x} \right)_{x=0} dt \tag{4}$$

$$c(x = L, t) = -\frac{nD_e}{H_c} \int_0^t \left(\frac{\partial c}{\partial x} \right)_{x=L} dt \tag{5}$$

where 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 boundary conditions in through-diffusion experiment are analogous to the field conditions. The Eqs. (1)–(5) are solved either using numerical or semi-analytical techniques to obtain theoretical contaminant concentration distribution with spatial distance and time [5, 14, 18, 35, 41, 43]. Due to the nature of the theoretical solution, the design parameter estimation using inverse analysis is computationally inefficient [9]. A closed-form analytical solution for transient through-diffusion problem was developed by Bharat [8, 9] using the method of Laplace transformation and integral theorem. The solution at the boundaries is given by

$$\frac{c(x = 0, t)}{c_0} = \frac{1}{2 + K} + 2K \sum_{j=1}^{\infty} \frac{(\alpha_j^2 + K^2) e^{-\alpha_j^2 T}}{4\alpha_j^2(K + 1) - (2K - (\alpha_j^2 - K^2))(\alpha_j^2 - K^2)} \tag{6}$$

$$\frac{c(x = L, t)}{c_0} = \frac{1}{2 + K} - 2K \sum_{j=1}^{\infty} \frac{(\alpha_j^2 + K^2) e^{-\alpha_j^2 T}}{4\alpha_j^2(K + 1) - (2K - (\alpha_j^2 - K^2))(\alpha_j^2 - K^2)} \tag{7}$$

where $K = \frac{nR_d}{H_r}$, $T = \frac{tD_e}{R_dL^2}$, H_r is the equivalent height of the source and collect reservoirs, α_j are the eigen values of the following transcendental equation

$$\tan \alpha_j = \frac{2K\alpha_j}{\alpha_j^2 - K^2} \tag{8}$$

where α_j are the roots of the aforementioned equation. The eigen values of the Eq. (8) were obtained using a discontinuous, multimodal optimization algorithm using Glow-worm swarm optimization technique [7]. The closed form solutions in Eqs. (6)–(7) were evaluated using first 20 number of roots using the optimization technique. The inverse problem of determining the diffusion coefficient and linear retardation factor was solved by minimizing the

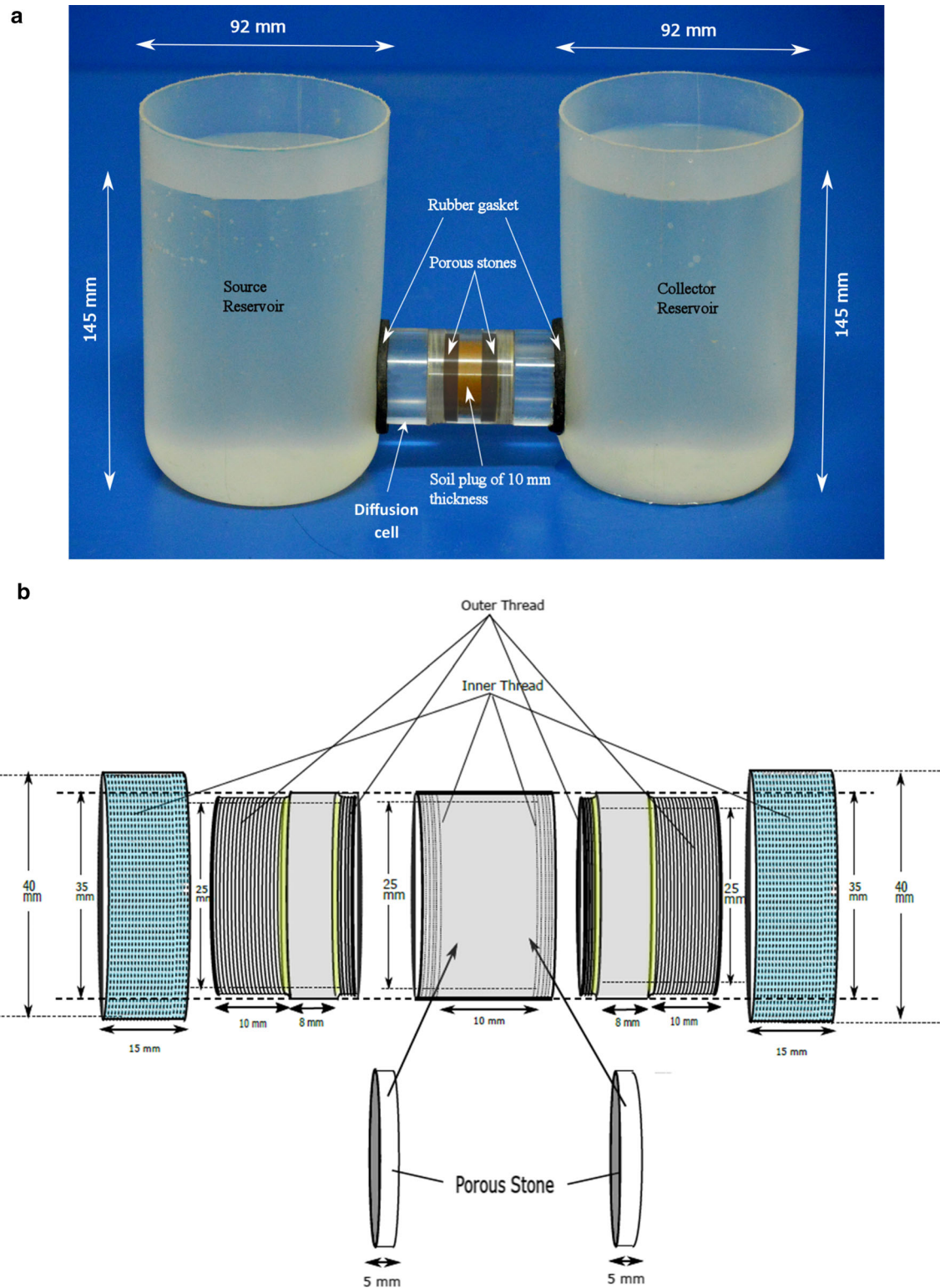


Fig. 1 a Laboratory through-diffusion set-up used in the current study. b Dimensional details of the diffusion cell used in the through-diffusion set-up

error between theoretical and measured concentration data in the source and collector reservoirs at different time intervals. The minimization was accomplished by particle

swarm optimization technique [9, 13, 15]. A Java-based software package, CONTRADIS, incorporates the aforementioned forward and inverse analyses, was used in this

Table 2 Data showing cation properties of the studied slats and estimated design parameters

| Salts | Molecular weight (g/mol) ^a | Hydrated radius (Å) ^a | Valence | D_e (m ² /sec) | R_d |
|--------------------|---------------------------------------|----------------------------------|---------|-----------------------------|-------|
| Lithium chloride | 42.394 | 7.3–10.3 | 1 | 1.57×10^{-10} | 13.01 |
| Sodium chloride | 58.44 | 5.6–7.9 | 1 | 6.35×10^{-10} | 7.71 |
| Potassium chloride | 74.55 | 3.8–5.32 | 1 | 8.92×10^{-10} | 8.91 |
| Calcium Chloride | 110.98 | 9.6 | 2 | 1.04×10^{-9} | 10.87 |

^a Sridharan and Prakash [51]

work. The non-commercial software, CONTRADIS, is developed at IIT Guwahati, recently by Partha Das et al. [21]. The model parameters for all the experiments were obtained by inputting the experimental measurements.

Results and Discussion

The measured data from the diffusion experiments were presented as relative concentrations, c/c_0 , by normalizing the measured concentration with initial concentration, $c_0 = 0.2$ M. The measured concentration data in source and collector reservoirs with time for different salts were presented in Fig. 2. The salt concentration in source reservoir decreased with time and the concentration increased with time in the collector, for all the salt solutions. The diffusion rate of Li cations through clay plug was observed to be very slow compared to others cations. The relative concentration of LiCl in source reservoir was ~ 0.8 after 2 months of diffusion period whereas the relative concentration of KCl and CaCl₂ reached ~ 0.5 by this time, indicating the completion of the test. The NaCl concentration in the source was ~ 0.6 at the end of 60 days which was between the diffusion rates of LiCl and KCl. The diffusion rate of KCl was faster than CaCl₂ in the beginning, but with time the rate was similar for both the salts. The difference in the relative concentration and diffusion rates at any given time indicate the cation complexation on the mineral surface. The LiCl was absent in the collector reservoir for initial 10 days indicating a strong adsorption on the mineral surface due to cation exchange and slower diffusion rates through the plug. The relative concentration of other cations was present in the collector nearly after 3 days.

The measured data was used to determine the diffusion and linear sorption parameters by inverse analysis. The model parameters obtained by minimizing the error between measured and theoretical concentration data for different salts were presented in Table 2. The theoretical concentration data using the optimized design parameters (Table 2) for different salts were given in Fig. 3a–d. The theoretical concentration data obtained using the

optimized model parameters by CONTRADIS were in good agreement with the measured concentration data for all the cases presented. However, a slight deviation between the measured and theoretical data was noticed in the beginning of the diffusion testing ($t \leq 10$ days) monovalent cations. The deviation was mainly due to cation exchange process in the initial stage of the diffusion as a significant percentage of calcium ions were present, in the exchangeable state, for the studied bentonite. The sorption mechanism is, therefore, expected to be highly complex, but the deviation was not significant and considered mechanism was appropriate for these cases. The theoretical data was in very good agreement with the measurements for CaCl₂.

The hydrated cation size and molecular weight of the studied salts were given in Table 2. The diffusion coefficient increased with the decrease in the hydrated cation size. The decrease in the diffusion coefficients with increase in the radius can be qualitatively understood from the diffuse double layer (DDL) theory. The DDL thickness increases with the increase in the cationic radius of the same group (i.e., valence) in the periodic table [34, 39]. The increase in the DDL thickness in a compacted state, where the volume change was not allowed, reduces the mobility of the cations. The diffusion coefficient, therefore, decreased. As the retardation considers the retention mechanism along with the adsorption and absorption

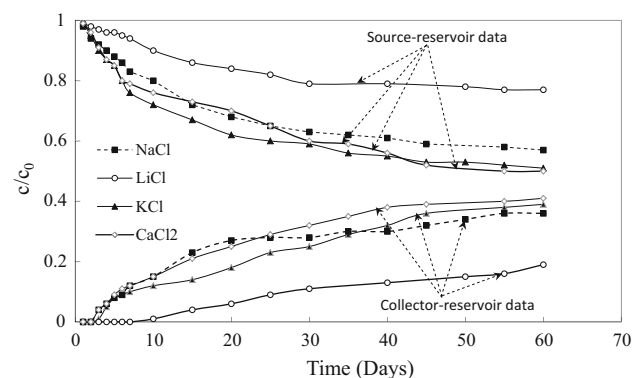


Fig. 2 Temporal data of measured salt concentration in source and collector reservoirs

processes, the R_d was higher for the lithium. The diffusion coefficients of lithium and potassium differed by nearly one order magnitude. More number of free paths was available in case of KCl due to the presence of smaller DDL thickness around the clay platelets. The diffusion coefficients of KCl and CaCl_2 , however, were nearly the same, which was also evident from the concentration profiles in Fig. 3c, d. The observed trend was in agreement with the earlier observation made by Sridharan et al. [52] on the compressibility behavior of homoionized bentonites, using potassium and calcium. The retardation factor for CaCl_2 was higher compared to KCl due to preference for higher valence cations on the mineral surface to effectively utilize the surface density [1, 39].

The significance of the estimated mass transport parameters on the linear design was analyzed by considering the spatial distribution of the considered inorganic species at a given time. Theoretical data of salt concentration variation with depth after 5 years was simulated using the estimated mass transport parameters in Fig. 4 using the following expression [46].

$$\frac{c}{c_0} = \exp \left[\frac{nR_d x}{H_f} + \left(\frac{n}{H_f} \right)^2 D_e R_d t \right] \tag{9}$$

$$\operatorname{erfc} \left[\frac{x}{2\sqrt{D_e t/R_d}} + \frac{n}{H_f} \sqrt{D_e R_d t} \right]$$

where all the above terms have the same meaning as described in Eqs. (1)–(4).

Equation (9) simulates the concentration profile for semi-infinite boundary condition at the bottom and flux boundary condition (Eq. 4) at the top boundary. The simulated data showed that a significant variation in the concentration data of different salts was found with depth. The LiCl salt solution could not migrate 20 cm depth of the clay liner even after 5 years, but a small concentration of other salts was available at 50 cm depth at the same time. The diffusion migration of Li^+ was significantly slower than other cations due to the presence of thicker DDLs.

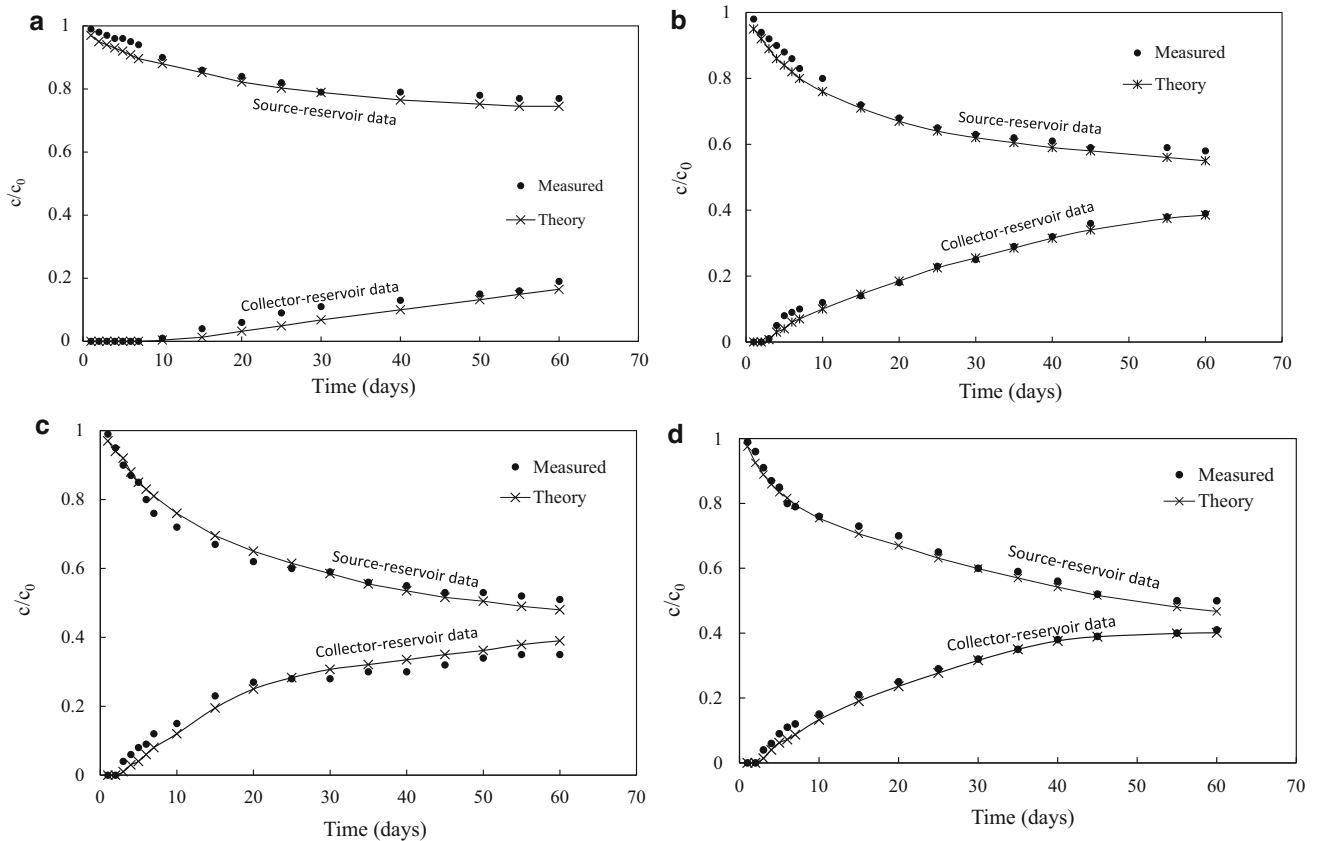


Fig. 3 a Comparison of the experimental concentration profile with the theoretical data for LiCl. b Comparison of the experimental concentration profile with the theoretical data for NaCl. c Comparison of the experimental concentration profile with the theoretical data for

KCl. d Comparison of the experimental concentration profile with the theoretical data for CaCl_2

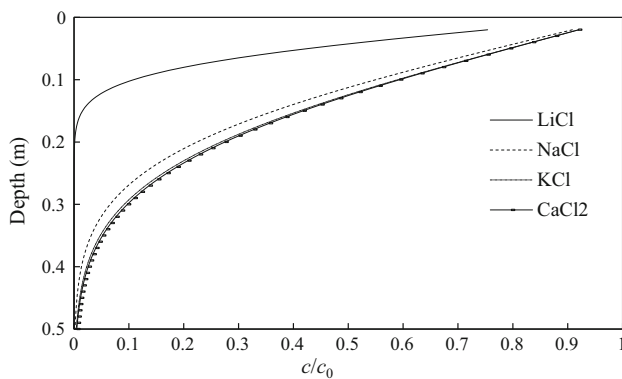


Fig. 4 Simulated spatial variation of salt concentrations with depth through clay liner after 5 years with the predicted design parameters

Conclusions

The diffusion coefficient of a compacted bentonite was significantly influenced by the hydrated size and valence of the migrating counter ions. Diffuse double layer theory was useful to qualitatively analyze the mass transport parameters of compacted plastic clays due to the influence of salt migration. The diffusion coefficient decreased with the increasing in size of the hydrated cations due to increase in the diffuse double layer thickness around the clay platelets. The diffusion coefficient of the studied bentonite was about one order smaller for LiCl compared to KCl at the same concentration and initial compaction density. The diffusion coefficient of bentonite with CaCl₂ and KCl were nearly the same. The effect of smallest hydrated radius and higher valence was similar on the migration paths in the clay pore space. The variation in the diffusion coefficient due to cation size was significant in the design of liners. The present study is, further, very useful in understanding the consolidation induced diffusion studies.

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