

Evaluation of Organoclays for Use in Landfill Liners

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Abstract: Organoclay obtained from two constituents' coco-dimethyl benzyl ammonium chloride, and bentonite was used in this study to prepare five admixtures, by varying the amount of organoclay, natural soil, and bentonite. Laboratory experiments were conducted on these admixtures with the objective of identification and assessment of their potential for use in landfill liners. The admixtures had the organoclay ranging from 10 to 25%, and bentonite in the range of 0 to 20%. The admixtures prepared were evaluated by conducting laboratory sorption tests and permeability tests for the determination of retardation coefficient, and hydraulic conductivity. Permeability tests were conducted using consolidation permeameter. Total Organic Carbon (TOC) was determined using TOC Analyzer. Admixture with higher percentage of organoclay exhibits higher organic sorption capacity. Retardation coefficient of the admixtures was determined by curve fitting the experimental data of sorption tests to fit to Freundlich (nonlinear) sorption isotherm. One-dimensional transport simulations were performed to evaluate completely the effectiveness of these materials for use as landfill liner and to develop design charts for determining required liner thickness.

Keywords: Organoclay, landfill, groundwater, contaminant transport, liner thickness.

INTRODUCTION

Leachates from municipal solid waste (MSW) and hazardous waste disposal facilities contain a wide range of potential environmental contaminants. In order to protect underlying groundwater resources from these contaminants, waste disposal sites are commonly lined with compacted clay or a composite liner consisting of compacted clay and geomembrane. The design of these liner systems is focused on minimizing the flow rate of leachate through the liner. Generally, compacted soil liner in the thickness of 1 to 1.2m is considered adequate to minimize the rate of contaminant migration by reducing the advective transport of contaminants through the liner. However, even with hydraulic conductivities less than 10^{-7} cm/s, the mass flux of many organic contaminants across compacted clay or composite liners by diffusion can be significant [1, 2]. Contaminants can migrate through clay by simple Fickian diffusion at rates that can be significant. Diffusion may result in early breakthroughs (less than 30 years) and large contaminant fluxes in typical clay liners [3-5]. Diffusion involves movement of a chemical species from a region of high concentration to a region of low concentration. If a liner system is placed into the position, the only way to reduce the effect of diffusion is to reduce the concentration gradient by contaminant retardation. Because of the inability of composite landfill liners to impede diffusive transport, enhancement of the sorption capacity of earthen liner materials is considered as a means to improve liner performance. The magnitude of organic contaminant sorption to natural soils and clays is related to the organic solute's aqueous solubility and the organic-carbon content of the sorbent [6, 7]. Sorption efficiency of modified clays for organic contaminants increases with the increase in

number of carbon atoms associated with Quaternary Ammonium Cations [8]. The natural soils and clays typically have organic-carbon contents less than 0.5%. A method of enhancing organic contaminant sorption and thus minimizing the flux of leachate contaminants through earthen liners is to amend the liners with materials capable of strongly sorbing organic contaminants.

The replacement of inorganic cations such as sodium in clay minerals by quaternary ammonium cations through the cation exchange reaction reduces the hydration of the clay and decreases its surface negative charge. As a result, the surface properties of the clay change significantly from being highly hydrophilic to increasingly organophilic. The sorption characteristics of clays modified by quaternary ammonium compounds, called organoclays to ionic and non-ionic organic compounds are mainly due to the partitioning process or hydrophobic interactions [9, 10]. Organoclays effectively minimized the impact of phenolic wastes on cement hydration [11]. The study on organoclays as waste containment barriers for pollutant attenuation showed that they were very attractive alternatives to the conventional clay liners [12, 13]. Increasing the sorption capacity of the earthen liner effectively reduces the contaminant advection velocity and the rate of solute diffusion during transient solute transport without requiring an increase in liner thickness [14, 15]. Although a sorbed contaminant will eventually desorb from the liner, the mass flux from the bottom of the liner is significantly reduced when an organobentonite is a component of the liner [16].

The objective of this study was to investigate the potential use of organoclays with soil-bentonite admixtures in retarding the movement of contaminants, while maintaining required permeability specifications thereby reducing the liner thickness. In order to evaluate the potential effectiveness of sorptive materials as amendments to clay liners, sorption and permeability tests were performed on five admixtures obtained by

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adding varying amount of the organoclay to the natural soil, and bentonite. One-dimensional transport modeling was performed to determine how effective each of these admixtures would be at retarding the transport of organic contaminants if used as landfill liner. The required barrier thickness is also determined using design charts developed from a one-dimensional contaminant transport model.

MATERIALS & METHODS

Liner Materials

Three liner materials; natural soil, bentonite clay, organically modified clay, were used in this experimental work. The natural soil selected to be used in this work was obtained from Delhi, having yellowish color. The natural soil obtained was oven dried at 103°C for three days, and then passed through a 600 micron sieve after breaking the clods. The soil passing through the sieve was collected and used in the experimental work. Bentonite clay used was saturated with sodium. Organoclay used in the study was obtained by modifying the bentonite by addition of coco dimethyl benzyl ammonium chloride. Small amount of ultra pure water was first added to the bentonite clay. The clay was then added to the coco dimethyl benzyl ammonium chloride with more amount of ultra pure water. Entire contents were mixed in a pug mill in laboratory. Mixed contents were kept in oven and a temperature of 102 °C was maintained for 48 hours, followed by grinding and sieving of the contents.

This study involved preparation of five kinds of soil admixtures (M1, M2, M3, M4, M5) using the organoclay prepared in laboratory. Organoclay, natural soil, and bentonite were mixed in different proportions. These admixtures were subjected to batch sorption tests for Total Organic Carbon (TOC). Composition of five types of admixtures is shown in Table 2. Percentage of each constituent was taken on a dry weight basis. For assessing the organic sorption capacity of admixtures, the parameter Total Organic Carbon (TOC) was used. TOC was determined using TOC analyzer of the make analytic Jena, model multi N/C 2100. The gross organic term TOC was selected to reflect the overall organic removal ability of admixtures.

Bhalaswa Landfill

Organic sorption tests on admixtures prepared in laboratory were conducted using leachate sample obtained from Bhalaswa landfill site in Delhi. Bhalaswa Landfill site which is located in North Eastern part of Delhi came into operation in 1992. The landfill site occupies 40 acres of land that was once used for sugar cane plantation. The total volume available for waste containment is about 2.9 million m³. It is actually receiving 2400-2500 tons of wastes per day and at such rate, the expected active life of the landfill has almost been crossed. However, plans to extend the landfill site are underway. The landfill is publicly owned and is managed by Municipal Corporation of Delhi (MCD). Almost the entire quantity of wastes received at the landfill facility can be classified as municipal waste. Characteristics of leachate collected from landfill are shown in Table 1.

SORPTION TESTS

The TOC concentration in the landfill leachate was found to be 4890 mg/L. Batch sorption tests were conducted by the

Table 1. Characteristics of Leachate from Bhalaswa Landfill

Parameter	Concentration (mg/L)
Total suspended solids	620
Total dissolved solids	20,310
BOD ₅	4390
COD	10,170
Total Organic Carbon	4890
Chlorides	6,840
Fluoride	0.60
Total iron	8.20
Chromium	0.72
Lead	0.84
Zinc	3.2
Copper	0.80
Phenolic compounds	0.92
Cadmium	0.11
pH	8.3

addition of 5–40 g of each air-dried admixtures type individually into 60 mL of landfill leachate with TOC concentration of 4890 mg/L. To maintain the solution at neutral, a buffer solution containing 0.01M potassium dihydrogen phosphate and 0.001M sodium phosphate was added. The vials were then mixed by subjecting them end-over-end rotation using a tube rotator for 24 h. The supernatant (700 µL) was withdrawn, filtered, and placed into vials. Each test was repeated thrice. Blanks contained 60 mL of 4890 mg/L of TOC solutions. The blanks in TOC showed equilibrium concentration of 4890 ± 24 mg/L, indicating no significant loss of TOC in the blanks. For the stock solution of TOC, 10.627g of anhydrous potassium biphthalate (C₈H₅KO₄) was dissolved in carbon free ultra pure water and diluted to 500 ml (1.0 ml = 10 mg of organic carbon). Calibration curve was prepared by diluting the stock solutions to cover the range of TOC from 0 to 5000 mg/L using TOC analyzer. The experimental batch sorption data were fit to the nonlinear Freundlich isotherm $S = K_f C^b$ using software LabFit, where S is the mass of solute removed from solution per unit mass of soil (mg/g), C is equilibrium concentration (mg/L), and K_f and b are the parameters determined from best fitted curve.

PHYSICAL AND HYDRAULIC PROPERTIES

Optimum Moisture Content (OMC) and Maximum Dry Density (MDD) for five types of admixtures were determined with Standard Proctor Test Method in accordance with IS 2720 (Part VII). The tests specimens, prepared using admixtures, were allowed to hydrate for 24 hours. The specimens were compacted at varying moisture contents in a 100 mm diameter mold with a 2.6 Kg weight rammer dropped from a height of 310 mm. The hydraulic conductivity test was performed using consolidation permeameter. The specimens were compacted at 3% wet of optimum water in accordance with standard procedures for the construction of compacted clay liners for waste containment. The compacted

specimens were extruded from the compaction mold, and tested for permeability in consolidation permeameter.

Table 2. Compaction Properties of Admixtures

Admixture	Percent Component in Admixture			Compaction Properties	
	B	O	NS	OMC	MDD
M1	15	10	75	25.2	1480
M2	10	15	75	31.0	1350
M3	15	10	75	35.2	1340
M4	20	15	65	36.8	1270
M5	20	20	60	38.1	1255

B- Bentonite, O- Organoclay, NS- Natural Soil.

RESULTS & DISCUSSION

TOC sorption for the five soil admixtures with different proportions of natural soil, bentonite, and organoclay were studied using batch sorption tests. The tests were carried out at pH 7 and temperature $25 \pm 1^\circ\text{C}$. Fig. (1) shows the sorption isotherms of the TOC from the leachate onto the five types of admixtures. Each sorption data is average of three values of absorption. All the sorption curves can be seen having initial convexity and a final upsweep. Such sorption behavior is indicative of weak adsorbent-adsorbate interaction at low concentrations, but once a molecule becomes adsorbed, adsorption of more molecules gets promoted in a cooperative fashion. It can be observed from the figures curves that the TOC sorption follows a pattern dependent on the composition of soil admixture (Fig. 1). The soil admix-

ture having a higher content of organoclay has higher sorption capacity for TOC. The admixture M1 which is composed of 25% organoclay and 75% natural soil has maximum sorption capacity for TOC, and the admixture M3, which is composed of 75% natural, 15% bentonite, and 10% organoclay has minimum sorption capacity for TOC.

Since the sorption isotherms are nonlinear, the partition coefficient, K_f , is not constant but is a function of the equilibrium concentration of TOC. The variation of partition coefficient with equilibrium concentration depends on the isotherm shape. The slope of a convex isotherm at a lower concentration is smaller than that at a higher concentration. It is difficult to make use of a non uniform partition coefficient in a one-dimensional contaminant transport model. An approximation of a representative linear partition coefficient is therefore essential based on weight-mean method [17]. With the weighted-mean method, the average value of the partition coefficient, K_f and the retardation factor, R , are estimated using following equations:

$$K_p = \frac{\int_0^c \frac{\partial S}{\partial C} dC}{\int_0^c dC} = \frac{\int_0^c K_f b C^{b-1} dc}{\int_0^c dC} = K_f C^{b-1} \tag{1}$$

$$R = 1 + \frac{\rho K_f C^{b-1}}{n} \tag{2}$$

where ρ is bulk density of the soil in kg/m^3 and n is soil porosity. The retardation factor calculated at $C=0.5C_0$ is shown in Table 3. The reason for using $C=0.5C_0$ is because it is more representative of the equilibrium concentration of TOC. The physical meaning of R in this case can be defined

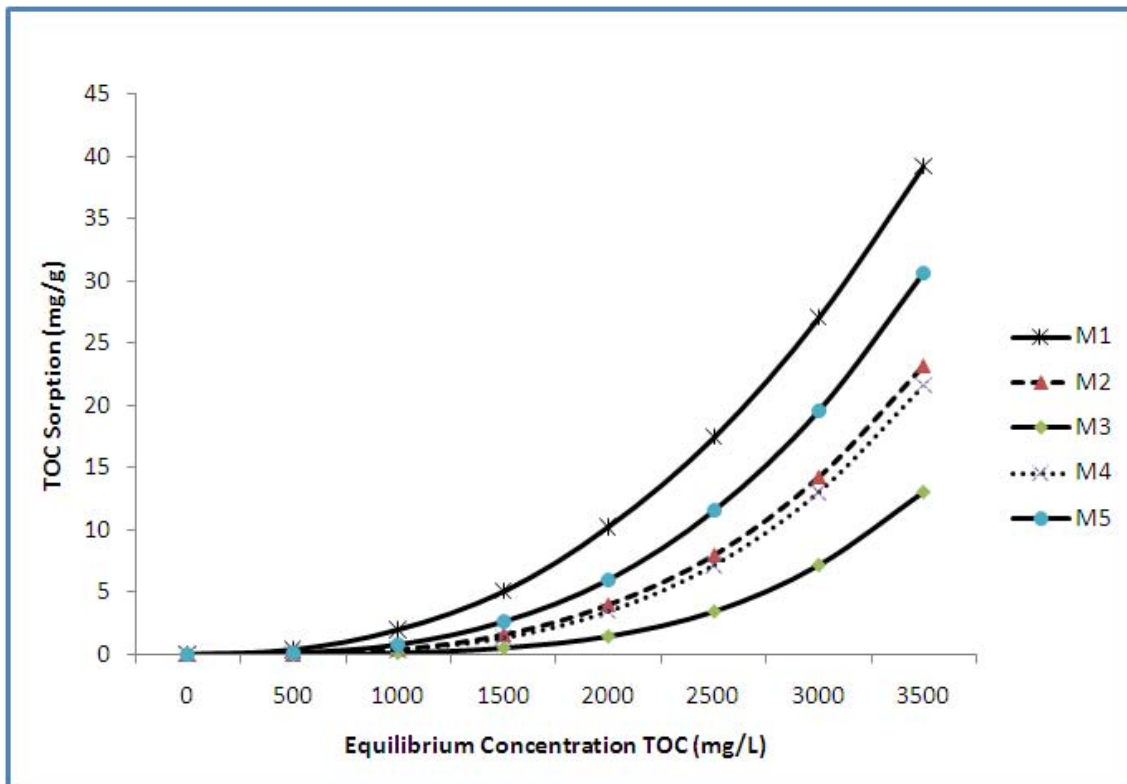


Fig. (1). Sorption Isotherms (TOC).

as the ratio of the time required for a contaminant to attain a half-maximum concentration, as compared with that for a conservative tracer.

Table 3. Sorption Isotherms for TOC

Admixture	Freundlich Isotherm	R	Correlation r ²
M1	$7.13 \times 10^{-9} C^{2.78}$	21.59	0.978
M2	$1.56 \times 10^{-10} C^{3.15}$	9.08	0.966
M3	$2.1 \times 10^{-13} C^{3.89}$	4.20	0.963
M4	$5.21 \times 10^{-11} C^{3.27}$	7.51	0.966
M5	$1.59 \times 10^{-9} C^{2.90}$	12.18	0.980

It can be observed from Table 3 that admixture M1 with 25% organoclay has the larger retardation factor, which matches with the trends in sorption isotherms. Similarly, the admixture M3 with minimum percentage of organoclay (10% in this case) has least retardation factor. The physical properties and measured hydraulic conductivity of each soil admixture are shown in Table 4. The soil admixtures M1 to M5 have a porosity ranging from 0.43 to 0.47. Similar studies carried out showed retardation factors varying between a minimum of 2.74 to a maximum of 12.49 for a corresponding content of modified clay of zero and 20% respectively [14].

The cost of replacing the traditional compacted clay liner would involve the material and technology cost, both of which are expected to be marginal, making the total cost of substitution to be only marginally higher. However, the additional costs for such replacement would be offset by the benefits achieved from in the form of (i) avoidance of remediation cost for cleaning up of contaminated groundwater (ii) environmental benefits achieved in the form of reduced risk of human exposure to contaminated water, thus avoiding human health cost. Complete cost benefit analysis of the use of organically modified clay in landfill liners is thus a complex issue, which can be suitably addressed only by analytical tools and models of environmental economics, and is beyond the scope of this paper.

Table 4. Physical & Hydraulic Properties of Soil Admixtures

Admixture	γ	n	k
M1	1242	0.46	1.4×10^{-7}
M2	1210	0.45	8.0×10^{-8}
M3	1158	0.47	4.7×10^{-8}
M4	1119	0.44	1.8×10^{-8}
M5	1104	0.43	1.6×10^{-8}

γ - Density (kg/m^3) n - porosity.
 k - Hydraulic conductivity (cm/sec).

TRANSPORT MODELING SIMULATIONS

The experimental results from the sorption and permeability experiments were used as an input data for transport simulations in order to evaluate the potential benefit of using sorptive amendments as a component of compacted clay

liners. The transport of dissolved contaminants through porous media can be described by equation that describes mass transport of contaminants as a result of water movement, hydrodynamic dispersion, and sorption. Mass transport of contaminants represented by Eq. (3) simply states that the increase in contaminant concentration within a small region is equal to the accumulation of mass due to advective-diffusive transport minus the decrease in mass due to reaction/sorption:

$$\frac{\partial C}{\partial t} = \frac{D_h}{R} \frac{\partial^2 C}{\partial z^2} - \frac{v_s}{R} \frac{\partial C}{\partial z} \quad (3)$$

where, C = Contaminant concentration at any depth z and time t in the liner; z = depth measured from top of the liner; D_h = hydrodynamic dispersion coefficient, m^2/year ; v_s = advective velocity, m/year ; R = retardation coefficient, calculated from sorption data and soil properties. The hydrodynamic dispersion coefficient, D_h in Eq.3 is often expressed as sum of the effective molecular diffusion coefficient, D_e , and mechanical dispersion coefficient D_m ; $D_h = D_e + D_m$. Previous studies indicate that the hydrodynamic dispersion coefficient can be regarded as the effective molecular diffusion coefficient under very low seepage velocity conditions, as is typically observed in clay liners. In other words, diffusion can be the dominant a mass transport process in clay liners. The contaminant interaction with the liner material is usually accounted for the retardation factor, R , which represents the relative rate of fluid flow to the transport rate of a reactive contaminant and can be determined using batch sorption tests. For non-reactive contaminants such as chloride, the retardation factor is unity and the solute is transported at the rate of the advective velocity. However, for reactive contaminants, the retardation factor is greater than unity and the solute is transported at a rate slower than that of the advective velocity.

For a given values of v_s , R and D_h , the concentration distribution of a single species at any time t and space z can be determined by solving Eq. (3) with a set of boundary conditions. To solve the 1D pollutant transport equation through a low permeability liner at a waste disposal facility, the following boundary and initial conditions can be imposed:

$$\text{Initial condition: } C(z,0) = 0; \quad (4a)$$

$$\text{Top of the liner: } C(0,t) = C_0, \quad (4b)$$

$$\text{Bottom of the liner: } \frac{\partial C}{\partial z}(\infty, t) = 0 \quad (5)$$

The boundary condition at the top of the liner is assumed to maintain a constant concentration. The top of the liner is assumed to have a continuous and infinite replenishment of solute. This is consistent with the fact that there is a virtually infinite source of mass in the waste and that any loss by transfer downward through the liner can be immediately replaced. The constant concentration condition is conservative in design, as it does not account for the reduction in the strength of the leachate generated from a landfill for many years. For the boundary condition at the bottom of the liner, it is assumed that the liner has an infinite thickness, where the exit boundary condition is defined as zero contaminant concentration for all times, which implies zero diffusive flux at the liner exit. The initial condition means that the concen-

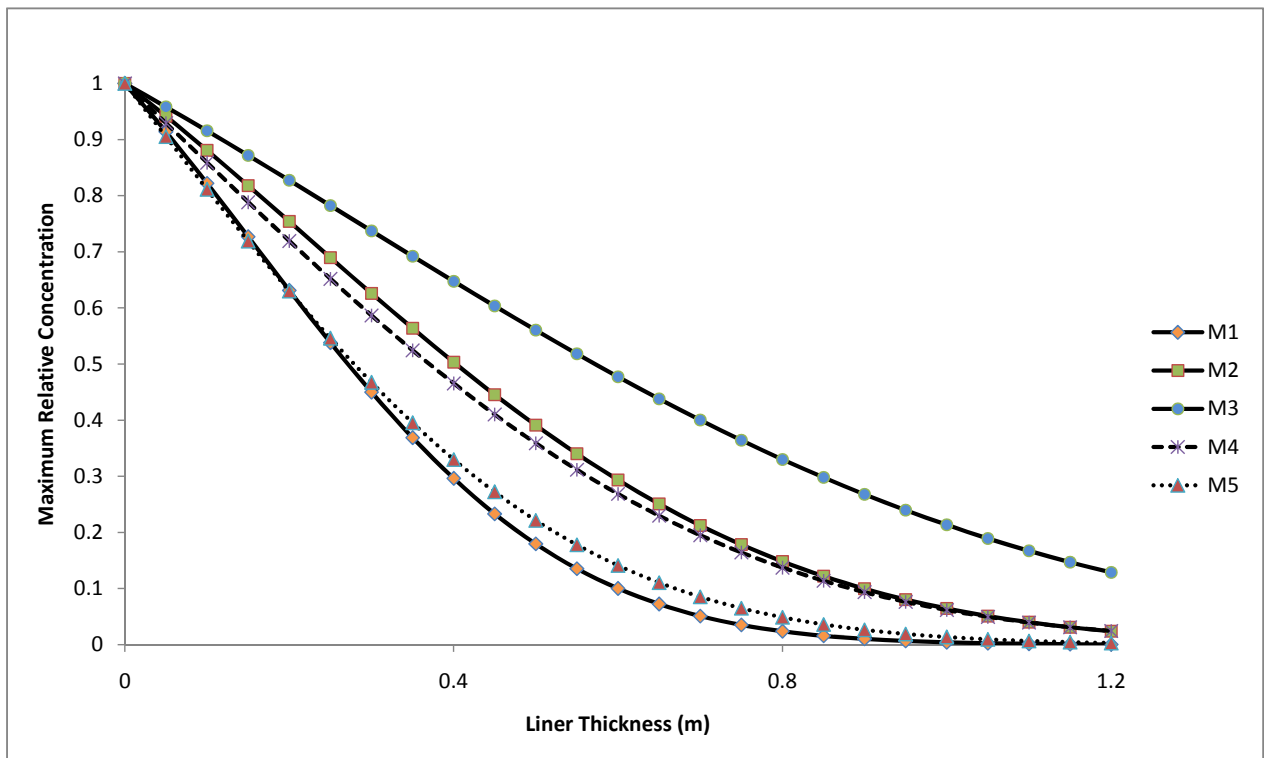


Fig. (2). Design chart for liner thickness.

tration of the contaminant is zero at any depth in the liner at time zero, which means that the liner may be assumed to be free of contaminant at the initial time.

Transport simulations were carried out using values of v_s and R determined in this study. For landfill liners, where mass transport is diffusion dominated; $D_h \cong D_e$ and may be taken as $0.02 \text{ m}^2/\text{year}$ for MSW landfills [18]. Total time period of simulation was taken as 50 years accounting for the first 10–15 years for waste receiving at landfill site and the remaining for post-closure. Eq. (3) representing transport of contaminants was solved using finite difference method implemented in MatLab 7.0. Simulation results were used for determining the maximum relative concentration at any depth within the liner and plotting the same. Simulations were carried for five types of admixtures. The results of simulation plotted in the form of graphs between maximum relative concentrations with respect to depth from the top of liner, can be used as design chart. Such chart can be utilized for the determination of liner thickness, if the maximum permissible relative concentration after a certain period of time is defined based on pollution prevention criteria in a region. Fig. (2) presnts a maximum relative concentration for a traveling time of 50 years for different admixtures. It is obvious that the required thickness is highly dependent on the retardation factor and hydraulic conductivity of the specimen. The required thickness for the admixture M1 is the least, as it has the highest retardation factor. Similarly, the required thickness for admixture M3 is the largest since it has the lowest retardation factor. Therefore, the only way to reduce the chemical flux is to improve the retardation factor of the soil material. The rule of thumb is that the larger the retardation factor of a liner material is, the lesser the liner

thickness. This, in turn, saves more space for landfill disposal of solid wastes.

CONCLUSIONS

In this study, both experimental work and simulation modeling were conducted. Experimental data on five soil admixtures, prepared by varying the content of organoclay and bentonite in natural soil, show that replacing 15% of bentonite with organoclay increases the retardation factor from 4.20 to 21.59. However, the presence of bentonite in soil specimen is also necessary, as it could reduce hydraulic conductivity of admixtures. A design chart was developed by solving 1D contaminant transport and mass transport equation by using finite difference technique. The chart provides a logical method for estimating the required thickness of a liner having composition based on these admixtures. The liner material with higher proportion of organoclay significantly reduces the required thickness because of the high sorption capacity.

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