

Laboratory determination of diffusion and distribution coefficients of contaminants in clay soil

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Abstract: A technique was described for determining the diffusion coefficients and distribution coefficients of contaminants passing through saturated clay samples. The technique was illustrated with reference to a number of laboratory tests involving diffusion migration of contaminants through a clayey soil of Shanghai, P.R. China. The mass of contaminant in the system was kept constant and so source leachate concentration decreased during each test. A simple theoretical model was used to analyze the test and it was shown that the diffusion coefficient and distribution coefficient from a single test could be deduced by Laplace transform method. Diffusion coefficients and distribution coefficients of Cl^- , K^+ , Ca^{2+} , Zn^{2+} , Cu^{2+} were calculated by Laplace transform program. It was shown that the apparent diffusion coefficient of anion Cl^- through the clay samples was much larger than those of cations, and the apparent diffusion coefficient of cation K^+ was smaller than those of divalent cations.

Key words: contaminant; migration; clay; diffusion; diffusion coefficient; distribution coefficient

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污染物离子在粘土介质中扩散系数和分配系数的测定

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摘 要: 介绍了利用一种自制的特殊装置, 测定污染物离子在粘土介质中迁移的扩散参数 D 和分配系数 K_d 的方法。通过一系列污染物在上海粘土中的纯扩散迁移试验, 系统中污染物的质量不变, 源浓度随试验的进行是下降的, 运用一个简单的理论模型, 通过拉普拉斯 (Laplace) 变换方法, 对一个单独的试验, 可同时推断出扩散系数和分配系数。通过拉普拉斯转换程序求出了阴离子 (Cl^-) 和阳离子 (K^+ , Ca^{2+} , Zn^{2+} , Cu^{2+}) 的扩散系数 D 和分配系数 K_d 。试验结果发现: 阴离子在粘性土壤中的显扩散系数比阳离子的大; 一价阳离子 K^+ 的显扩散系数比二价阳离子的大。

关键词: 污染物; 迁移; 粘土; 扩散; 扩散系数; 分配系数

0 Introduction

Owing to the limit of economic condition, the main disposal method of solid waste is still burying. The leachate of solid waste polluted soil and the surrounding underground water directly and indirectly, and cause a series of health problems to animals and human beings^[1]. In America, about 75 percent of waste landfills produce pollution to the surrounding water.

How to protect environment, and how to prevent the surrounding soil and water from pollution that comes from waste landfills is an important problem in building of waste landfills. The process of controlled contaminant migration through a clay barrier may provide a useful

means of attenuation. However safe design of these clay barriers will usually require both experiment and theoretical consideration of clay-leachate interaction and migration rates through the clay.

This paper describes a technique for determining the diffusion coefficients and distribution coefficients of contaminants passing through saturated clay samples. The advantage of this technique is that the migration process of contaminants in the system is diffusion only.

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A method to solve the diffusion model by a Laplace transform is developed, and the diffusion coefficients and distribution coefficients of Cl^- , K^+ , Ca^{2+} , Zn^{2+} , Cu^{2+} are calculated by Laplace transform program.

1 Basic concept and migration equations

The migration of contaminants through soil includes four forms: advection, dispersion, diffusion and sorption^[1], and is usually represented in one-dimensional partial differential equations. In "The Design of Waste Landfill"^[1], a migration equation is given as

$$\frac{\partial(\theta R c)}{\partial t} = \frac{\partial}{\partial x} \left[(\theta D \gamma + \alpha |v|) \frac{\partial c}{\partial x} - v c \right] - (\mu \theta c) \quad (1)$$

$\underbrace{\hspace{1.5cm}}_{\text{diffusion}} \underbrace{\hspace{1.5cm}}_{\text{dispersion}} \underbrace{\hspace{1.5cm}}_{\text{advection}} \underbrace{\hspace{1.5cm}}_{\text{decay}}$

where D is the diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$); R is the retardation coefficient; t is the migration time (s); v is the seepage velocity of underground water; x is the distance; α is the dispersion distance (m); γ is the hindrance factor; θ is the volumetric water content (m^3/m^3); μ is the decay coefficient.

In saturated clay media, if decay is ignored and a linear isotherm is appropriate, diffusion and dispersion can be combined together. Thus a more concise migration equation is given by^[2]

$$R_f \frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

where R_f is the retardation factor, $R_f = 1 + (\rho_b k_d / n)$, ρ_b is the dry density of medium ($\text{kg} \cdot \text{m}^{-3}$), k_d is the distribution coefficient of sorption isotherm ($\text{m}^3 \cdot \text{kg}^{-1}$), n is the soil porosity; other terms are the same as the above.

As represented in Eq. (2), in media of low permeability and in low flow conditions, the migration of contaminants is dominated primarily by diffusion. So the diffusion coefficient D is an important index of contaminant migration. Its value is important to the accuracy of the solution of differential equations.

In saturated clay media, if the hydraulic gradient is zero, seepage velocity equals zero. Eq. (2) can be simplified as

$$R_f \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (3)$$

The flux (f) of contaminants through a saturated porous medium can be approximated by a law in the form

$$f = nvc - D \frac{\partial c}{\partial x} \quad (4)$$

2 Laboratory tests

2.1 Test device

In order to determine the diffusion and distribution coefficients of contaminants in soil, a simple laboratory test device (Fig.1) was designed to simulate one-dimensional contaminant migration through a clay medium by diffusion only. This device was a rectangle box made up of porous polyethylene plastic plates of 0.3 cm in thickness. The device was divided into three parts by two polyethylene porous plates. The soil sample locates in the middle part and source of contaminants and distilled water in the other two parts respectively.

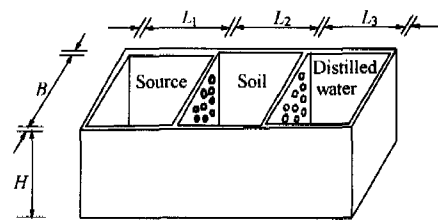


Fig. 1 Diffusion test device

Soil sample used here is shallow soil from Shanghai, P.R.China, having liquid limit w_L of 30.5% and plastic limit w_P of 18.9%. The sizes of the test device are as follows: $B = 10$ cm, $H = 15$ cm, $L_1 = 10$ cm, $L_2 = 10$ cm and $L_3 = 10$ cm.

2.2 Test method

A total of 5 tests (namely, Models 1~5) were conducted, the contaminants were ZnSO_4 , CuSO_4 , CaCl_2 , $\text{CaCl}_2 + \text{KCl}$ and NaCl respectively. Model 4 involved a source solution of both potassium and calcium chloride. Models 1~3 and 5 involved a single cation source solution. At the desired time (see Table 1), the concentration of contaminant at different points of soil sample was measured and analyzed by Tongji University Test Center. The concentration of Cl^- was measured by titration method and the concentration of cations (K^+ , Ca^{2+} , Zn^{2+} and Cu^{2+}) was measured by atom adsorption method.

The following were the test procedures. Firstly, soil was dried by air and used after sieving through a 2 mm sieve. Secondly, the soil prepared was put in the middle part of the device, rammed by gradationally, and the dry density of soil (ρ_d) and soil porosity (n) were measured (see Table 1). Thirdly, distilled water was added in other two parts of the device, so that the soil adsorbed water slowly and the air in pores of the soil was removed. This process lasted about half month to one month. After the soil samples in devices were saturated, the stock solutions

Table 1 Types of experiment

Model	Source	Initial concentration of source $c_0/(\text{mol} \cdot \text{L}^{-1})$		Dry density of soil sample $\rho_d/(\text{g} \cdot \text{cm}^{-3})$	Soil porosity n	Test period/d	Remarks
		Cation anion					
1	ZnSO ₄	0.1	0.1	1.50	0.43	63	$L_2=18 \text{ cm}$
2	CuSO ₄	0.1	0.1	1.50	0.43	63	(Mode 15)
3	CaCl ₂	0.1	0.1	1.50	0.43	63	$L_2=10 \text{ cm}$
4	CaCl ₂	0.1	0.2	1.50	0.43	63	(Modl 1~4)
5	+KCl	0.1	0.1	1.50	0.45	63	
	NaCl	0.1	0.1	1.45			

of Zn^{2+} , Cu^{2+} , Ca^{2+} , K^+ , Na^+ at a known concentrations c_0 prepared by dissolving ZnSO₄, CuSO₄, CaCl₂, KCl, NaCl in distilled water were added to the part of the devices with contaminants separately, and the distilled water was added to the part of the devices with distilled water. The liquid in these two parts should be at the same level in order to avoid advective flow of liquid. The source concentration decreased with time due to mass transfer into the soil according to the principle of mass conservation. After the desired time (see Table 1), the concentration of contaminant at different points of soil samples was measured.

3 Solution of the model

The test device here is a pure diffusion device. The migration equation which suits this model can be expressed with a one-dimensional migration equation in saturated media (Eq. (3)).

The boundaries in the tests here are as follows:

$$c(x > 0; t=0) = 0 \quad (5a)$$

$$c(x = 0; t = 0) = c_0 \quad (5b)$$

$$c(x = L; t > 0) = 0 \quad (5c)$$

Eq. (5a) means that the soil sample is free of contaminant at initial time ($t = 0$); Eq. (5b) means that the initial source concentration is a constant c_0 ; Eq. (5c) means that the contaminant concentration at the exit of the soil barrier is zero because of the presence of large amount of water.

$$c(0,t) = c_0 - \frac{1}{H_f} \int_0^t f(0,\tau) d\tau \quad (6)$$

The contaminant source concentration is reduced to account for transfer into the soil barrier.

In Eq. (6) $f(0,\tau)$ is the mass flux of this contaminant into the soil at time t ($f = -D(dc/dx)$); H_f is the height of source leachate, here $H_f = L_1$.

The migration of contaminant through the soil in the models is governed by Eqs. (3)~(6). An efficient and

convenient approach to solve these equations is to take Laplace transform of Eqs. (3), (4), (5c) and (6) and then find an semi-analytical solution in transforming space. For an initially uncontaminated barrier, the Laplace-Transformed solutions to Eq. (3) and (4) for concentration and flux have the following forms^[3]:

$$\bar{c} = B_1 \exp(\phi_1 x) + B_2 \exp(\phi_2 x) \quad (7a)$$

$$\bar{f} = nDB_1 \phi_2 \exp(\phi_1 x) + nDB_2 \phi_1 \exp(\phi_2 x) \quad (7b)$$

where B_1 and B_2 are the integration constants; ϕ_1 and ϕ_2 are the roots, defined as

$$\phi_1 = \frac{v}{2D} + \sqrt{\frac{v^2}{4D^2} + \frac{R_f s + \lambda}{D}} = \sqrt{\frac{R_f s}{D}} = \sqrt{\frac{s}{D^*}} \quad (8a)$$

$$\phi_2 = \frac{v}{2D} - \sqrt{\frac{v^2}{4D^2} + \frac{R_f s + \lambda}{D}} = -\sqrt{\frac{R_f s}{D}} = -\sqrt{\frac{s}{D^*}} \quad (8b)$$

B_1 and B_2 can be obtained according to the boundary conditions through the following process.

Taking a Laplace transform of Eq. (6) gives

$$\bar{c}_i = \frac{c_0}{s} - \frac{\bar{f}_0}{sH_f} \quad (9)$$

Combining Eqs. (7a) and (9) gives

$$B_1 \left(1 + \frac{nD\phi_2}{sH_f}\right) + B_2 \left(1 + \frac{nD\phi_1}{sH_f}\right) = \frac{c_0}{s} \quad (10)$$

Take a Laplace transform of Eq. (5c), and replace \bar{c} in it with Eq. (7a), then the following equation can be obtained:

$$B_1 \exp(\phi_1 L) + B_2 \exp(\phi_2 L) = 0 \quad (11)$$

The variation in concentration with depth or width and time can be obtained by combining Eqs. (10) and (11) to give

$$\bar{C} = \frac{c_0}{\exp(\sqrt{sR_f/D}x)} \frac{\exp(2\sqrt{sR_f/D}x) - \exp(2\sqrt{sR_f/D}L)}{s \left[1 - \exp(2\sqrt{sR_f/D}L) \right] - \frac{nD}{H_f} \sqrt{sR_f/D} \left[1 + \exp(2\sqrt{sR_f/D}L) \right]} \quad (12)$$

4 Experimental results

For any given set of D and R_f , the concentration at

any specified place and time can be obtained by numerically inverting the Laplace transform. When a test is finished at some time t , the concentration profile with x is determined. By adjusting the diffusion coefficient D and the distribution coefficient K_d , the Laplace solution outlined above may be matched to the observed concentration profile to give inferred values of both D and K_d . Eq. (12) is the solution in transforming space. It is necessary to invert the transform and find the solution in physical space. This can be done using a Laplace transform program. In this paper, a main program is compiled according to Eq. (12), and a Laplace transform subprogram is used. By adjusting the diffusion coefficient D and $\rho_b k_d$, the values of D and $\rho_b k_d$ matched to the results of the tests can be obtained. The results are given in Figs. 2~6 and Table 2. In Figs. 2~6, x represents distance away from source.

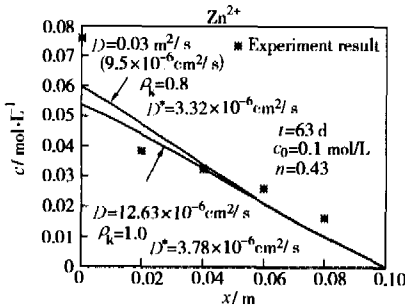


Fig. 2 The relationship between Zn^{2+} concentration and x

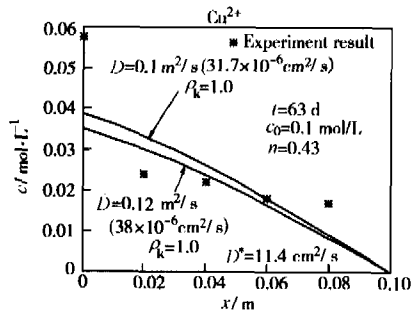


Fig. 3 The relationship between Cu^{2+} concentration and x

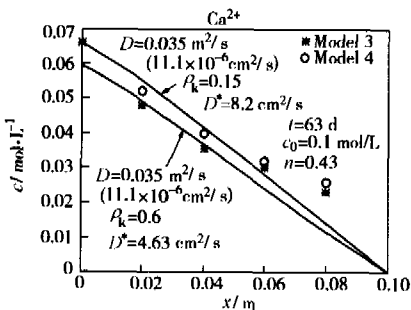


Fig. 4 The relationship between Ca^{2+} concentration and x

Figs. 2~6 indicate in models except Model 2, the theoretical curves conforms well to the experimental data.

It can be seen from Figs. 2, 3 and 5 that at the interface between the source and soil sample, there is a sudden change of concentration. Fig. 5 shows in multiple contaminant solution which involved $CaCl_2$ and KCl , cation K^+ has little effect on the diffusion coefficient of cation Ca^{2+} .

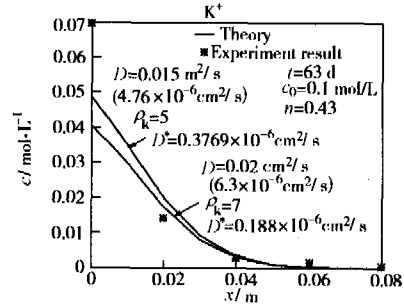


Fig. 5 The relationship between K^+ concentration and x

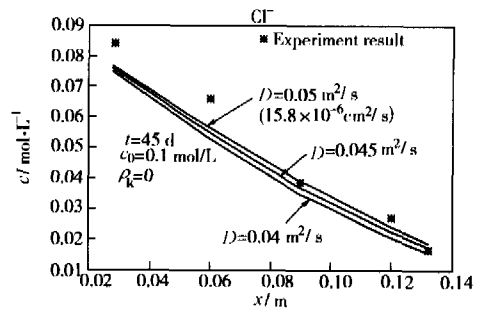


Fig. 6 The relationship between Cl^- concentration and x

5 Discussions

The diffusion of ions in soil porous media is affected by a series of factors, including the characteristics of ions, diffusion medium and environmental condition because of interaction between charged ions and charged soil particles.

The data in Table 2 show the following regularity. Firstly, the apparent diffusion coefficient D^* of anion Cl^- is larger than those of cations. This phenomenon can be interpreted by electrostatic action between ions and soil particles, which has been explained by the author in detail in Reference 4. Secondly, the apparent diffusion coefficient of monovalent cation K^+ is much smaller than that of divalent cations (Cu^{2+} , Ca^{2+} , Zn^{2+}). This is due to the appropriate size of cation K^+ ^[4]. Thirdly, the data in Table 2 also show that there is no regularity between the sizes of divalent cations (Ca^{2+} , Zn^{2+} , Cu^{2+}) and the values of diffusion coefficients or apparent diffusion coefficients.

The effect of companion ions on diffusion coefficients can be seen from Fig. 4. The results indicate

Table 2 Diffusion coefficients of ions

Ion	Diameter(Å)	$D \times 10^6 / (\text{cm}^2 \cdot \text{s}^{-1})$	$\rho_b k_d$	$D^* \times 10^6 / (\text{cm}^2 \cdot \text{s}^{-1})$	Results from References		
					$D \times 10^6$	$\rho_b k_d$	$D^* \times 10^6$
Zn ²⁺	0.074	9.5	0.8	3.3			3.0
Cu ²⁺	0.073	31.7,38	1.0	9.53,11.40			
Ca ²⁺	0.100	11.1	0.15,0.6	8.20,4.63	3.84	2.0	
K ⁺	0.151	4.76,6.3	5.0,7.0	0.38,0.19	6.3	7.0	
Cl ⁻		15.8	0	15.8	10.0	0	

Note: $D^* = D / R_f$, D^* is called apparent diffusion coefficient.

that presence of K⁺ has a little effect on the diffusion of Ca²⁺. The effect of companion ions on diffusion coefficients depends on many factors such as electric chemistry interaction between ions and ion concentration^[5].

Laboratory models of determining diffusion coefficients and distribution coefficients in laboratories are mostly column tests^[5-7]. The migration equation may take the form of Eq. (2) involving advection and diffusion. Rowe et al (1995)^[7] obtained the solutions in laboratory boundary conditions through Laplace transform. In application, by adjusting diffusion coefficient D and distribution coefficient K_d and matching the resulting theoretical curve to the experimental data it is possible to obtain an estimated D and K_d . The drawback of this approach is its complexity. The test model in this paper is very simple and the process of migration of contaminant in soil porous medium is a pure diffusion process in which there is no advection phenomenon. The author once determined the apparent diffusion coefficient by solving the Eq. (3) under the same test boundary conditions through an approximate method^[4]. But the shortcoming of that method is that the solution of the model don't conform very well to the test boundary conditions and only apparent diffusion coefficient D^* can be obtained.

The comparison between the results obtained in this paper and the results of laboratory column tests found in References is given in Table 2. But experimental data of Cu²⁺ hasn't been found. Diffusion results for a definite ion depend on many factors such as soil samples, test methods and environment conditions (i.e., temperature). For a definite soil, the diffusion is also affected by the size of soil particles, pH of soil, disturbed or undisturbed soil. The data in Table 2 show that results of Zn²⁺, K⁺ investigated in this paper are very close to the results of Zn²⁺, K⁺ found in References. But the results of Ca²⁺, Cl⁻ were somewhat different from the results in the

References.

The rationality of test results also has relation with the assumption of adsorption isotherm and the concentrations of contaminants. Because at relatively high concentration and nonlinear adsorption isotherm, the more appropriate migration equation is nonlinear advective-dispersive reactive equation. One-dimensional numerical solutions to this kind of equation are generally accomplished by traditional finite difference, finite element techniques and split-operator method^[8,9] that are still in exploration. The high D^* values for the cations are also attributed to the possibility of chemical precipitation of the heavy metal (Cu²⁺, Ca²⁺)^[8].

6 Conclusions

This paper has described a number of laboratory tests involving the diffusion migration of contaminants through a clay soil from Shanghai, P. R. China. A theoretical model was used to interpret the experimental results and to deduce appropriate diffusion coefficients and distribution coefficients of some cations (Zn²⁺, Cu²⁺, Ca²⁺, K⁺ and Na⁺) and anion Cl⁻. Based on this study, the following conclusions are made:

(1) The diffusion test device in this paper is simple and useful.

(2) The concentration in source leachate decreased during each test owing to contaminant migration into the soil, and it was shown that this phenomenon could be used to deduce both the diffusion coefficient and the distribution coefficient through the Laplace solution from a single test, and the results are relatively reasonable.

(3) For the conditions examined in these tests, the diffusion coefficients were as follows: for Ca²⁺, $11.1 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$; Zn²⁺, $9.5 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$; Cu²⁺, $(31.7 \sim 38) \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$; K⁺, $4.76 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$; Cl⁻, $15.8 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$. The dimensionless products $\rho_b k_d$, which measure the "sorption" of a particular contaminant species in

Shanghai clay, were as follows: for Ca^{2+} , 0.6; Zn^{2+} , 0.8; Cu^{2+} , 1.0; K^+ , 7; Cl^- , 0.

(4) The results show that the apparent diffusion coefficient D^* of anion Cl^- is larger than that of cations, and the apparent diffusion coefficient of cation K^+ is smaller than that of divalent cations.

In summary, the diffusion coefficients and distribution coefficients deduced from the tests by Laplace transform reported in this study are reasonable, and have some reference value.

It is noted that there are some disadvantages in the tests here. The first is that the sizes of the models should be larger. For example if L_2 and L_3 in Fig.1 became larger, the boundary conditions would be more suitable for the model in this paper and the results obtained would be more accurate and credible. The second is that the concentrations of source leachate should be lower so that the solutions of linear advective-dispersive reactive equation would be more reasonable.

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