

Determination of Diffusion Coefficient and Analysis of Diffusion Factors of Cr(VI) Ion in Clay Soil*

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Abstract: Some laboratory diffusion tests were conducted with diffusion device to determine the diffusion coefficient of Cr(VI) ion passing through Dalian red clay samples. The concentrations of Cr(VI) at different places of the samples were then measured spectrophotometrically after a standing time of 1 000 d. A one-dimensional solute transport equation was used to simulate the transport of Cr(VI) through clay samples. Back-calculation of diffusion coefficient of Cr(VI) was made with finite difference method. Parametric analysis was conducted to simulate variations in soil dry density, temperature, pH and standing time. The results show that the method used in this paper is simple and effective. The diffusion coefficient of Cr(VI) in Dalian red clay varies from 1.50×10^{-7} cm²/s to 2.08×10^{-7} cm²/s. After 1 000 d diffusion, the concentration of the source solution drops down to 1.27 mg/L from 62.5 mg/L, and the diffusion distance is only 3.5 cm. Under the assumption that diffusion coefficient is constant, the diffusion effect becomes more obvious with lower density, lower temperature, higher pH value, and much more time.

Keywords: landfill; Cr(VI) ion; transport; clay soil; diffusion coefficient

Due to the limit of economic condition, the main disposal method of solid-waste is still burying. Leachate from solid-waste landfills has been found to contain a number of harmful substances including heavy metals. These heavy metals may enter the aquifer underlying the landfill and thereby pose a potential threat to human health^[1]. To prevent the groundwater resource from being polluted, landfills are usually lined with clay liners. The main purpose of liner system is to minimize permeation of leachate through the liner. Although the permeability coefficient of liner system is less than 1×10^{-7} cm/s, many heavy metals can still pollute the groundwater by diffusion through a block liner^[2].

The migration of contaminants through soil includes four forms: advection, dispersion, diffusion and adsorption. In order to effectively predict the migration process of heavy metals in landfill clay liner, parameters such as seepage velocity, diffusion coefficient, and adsorption of

heavy metals onto clay must be confirmed properly. In many waste disposal places, such as sewage oxidation pond, water head difference between the inside and outside of the pond is small, and the water flow is not obvious. In these conditions, diffusion becomes the main control factor for contaminant migration through soil^[3]. Owing to the complexity of diffusion characteristics of contaminant ions and the importance of diffusion coefficient in theoretical research and barrier system design^[4], researches on testing method of diffusion characteristic deserve attention as there is little standard reference. However, most studies focus primarily on dispersion and adsorption^[5-8], and laboratory models of determining dispersion coefficient are mostly column tests^[9-11]. Studies on diffusion are relatively few. Xi *et al* did some laboratory tests to determine the diffusion coefficient of Cl⁻ and low valent cations in clay samples^[12]. However, the periods of laboratory tests are usually short, and studies on

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the diffusion coefficients of heavy metal anions and diffusion influencing factors are quite rare.

The objectives of this study were to measure the concentrations of Cr(VI) at different places of soil samples with diffusion test device after a long standing time, thereby to determine the migration rule of Cr(VI) ion simply under the effect of diffusion, and to analyze the effects of dry density, temperature, pH value and time on diffusion to provide reference for theoretical study and landfill design.

1 Testing materials and methods

1.1 Testing materials

The natural clay used in this study was obtained

from the Maoyingzi zone in Dalian city. The soil specimen had no history of exposure to Cr(VI). The chemical composition of the clay was 60.69% of SiO₂, 23.80% of Al₂O₃, 4.03% of K₂O, 2.03% of Na₂O, 0.23% of CaO, 0.30% of Fe₂O₃, 0.08% of MgO and 0.05% of TiO₂. The characteristics of the soil samples are given in Tab.1. The grain size distribution of the natural clay is shown in Fig.1. Potassium dichromate solution was used as a source of Cr(VI) in the diffusion tests. Chromium was selected as the test metal because of its commonness and high toxicity in landfill leachates.

In order to determine the diffusion coefficient of contaminant in soil, a simple laboratory test device (Fig.2) was designed to simulate one-dimensional contaminant migration through a clay medium by diffusion

Tab.1 Characteristics of the soil samples used in the tests

Permeability coefficient/ (cm·s ⁻¹)	Liquid limit/%	Plastic limit/%	Max. dry density/ (g·cm ⁻³)	Optimum water content/%	Porosity	Specific gravity
4.1×10 ⁻⁸	29.9	14.2	1.72	18.8	0.35	2.66

only. This device is a rectangle box made up of porous polyethylene plastic plates which is 1 cm thick. The device is divided into three parts by two polyethylene porous plates. The soil sample is located in the middle part and source of contaminant and distilled water in the other two parts respectively. The top of the device was sealed. After a standing time of 1 000 d, the concentrations of

contaminant at different places of soil samples were measured to determine the diffusion coefficient *D*. The sizes of the test device are as follows: *W* =10 cm, *H* =10 cm, *L*₁=10 cm, *L*₂= 5 cm, *L*₃=10 cm.

1.2 Testing method

Potassium dichromate solution was used as a source of Cr(VI) in the diffusion tests. The initial concentration of the source solution was 62.5 mg/L. The initial pH value of our test solution was adjusted to approximately 7.0 with dilute HNO₃ and NaOH, and the test was conducted in a constant temperature room of 295 K. The test procedures were as follows. Firstly, soil was dried by air and sieved through a 2 mm sieve. Secondly, the soil prepared was put in the middle part of the device, rammed gradationally, and the dry density of soil ρ and soil porosity *n* were measured (see Tab.1). Distilled water was added in the other two parts of the device, so that the soil adsorbed water slowly and the air in pores of the soil was removed. Thirdly, after the soil sample in devices was saturated, the stock solution of Cr(VI) and distilled water were added in these two parts of the device respectively. The water levels in these two parts should be of the same value in order to avoid advective flow. After a standing time of 1 000 d, the soil sample was sliced into 15 sublayers using a stainless steel thread. The pore water was extracted from the slices under 10 kPa pressure for 12 h. Afterwards, the slurry was centrifuged at a speed of

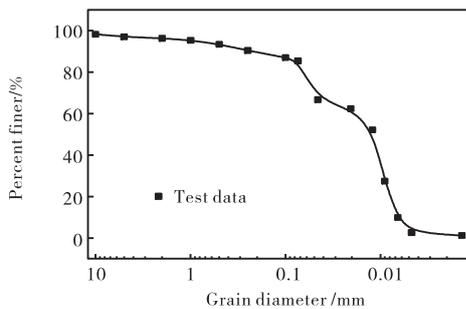


Fig.1 Grain size distribution of natural clay

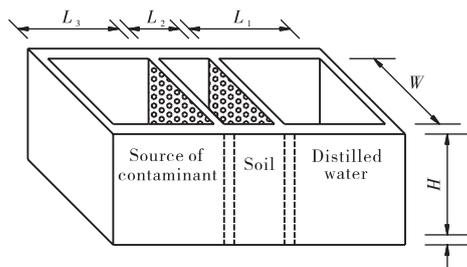


Fig.2 Diffusion test device

10 000 r/min for 30 min to obtain the supernatant. The spectrophotometer was then used to determine the Cr(VI) concentration at different places of the soil samples.

Batch tests were conducted to investigate the adsorption behavior of Cr(VI) at different temperatures and pH values. Dry soil samples 2—12.5 g and 25 mL aqueous solutions of different concentrations of Cr(VI) were mixed in each flask. The sample flasks were then put into a temperature-controlled shaking box which was rotated at 160 r/min. After different adsorption time, the slurry was centrifuged at a speed of 5 000 r/min for 5 min to obtain the supernatant. The concentration of Cr(VI) in the supernatant solution was then measured spectrophotometrically. The concentration of Cr(VI) adsorbed onto the soil solids was calculated from the mass balance,

$$q_t = \frac{C_0 - C_t}{M} V \quad (1)$$

where q_t is the amount of Cr(VI) adsorbed onto the soil samples at time t ; C_0 the initial concentration of Cr(VI); C_t aqueous phase concentration of Cr(VI) at time t ; V the volume of the aqueous phase; and M the mass of the soil samples.

1.3 Transport modeling simulations

Based on the migration mechanism of contaminant in porous medium, a one-dimensional migration equation is given as^[13]

$$n_e \frac{\partial C}{\partial t} + \rho \frac{\partial S}{\partial t} + n_e \left(v \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} \right) = 0 \quad (2)$$

where v is seepage velocity; n_e effective porosity; C contaminant concentration in the aqueous phase; D dispersion coefficient; S equilibrium adsorbed concentration; ρ dry density; t time; and x distance from the domain entrance.

The results of the batch tests were used as input parameters and the Langmuir model was found to fit well to the test data based on calculated correlation coefficients. For this study the adsorption model of Cr(VI) on all soil samples was a Langmuir isotherm model of the form^[14]

$$S = \frac{q_m b C}{1 + b C} \quad (3)$$

where b and q_m are isotherm parameters.

Combining Eq.(2) and Eq.(3) gives a one-dimensional migration equation of contaminant in soil as

$$\left(1 + \frac{\rho q_m b}{n_e (1 + b C)} \right) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (4)$$

D in Eq.(4) can be expressed as $D = D_m + D^*$, where D_m is a mechanical diffusion coefficient, $D_m = \alpha_L v$, α_L is longitudinal dispersivity, whose value is generally given as the average particle size; D^* is a diffusion coefficient. If the hydraulic gradient is zero, the seepage velocity equals zero. Eq.(4) can be simplified as

$$\left(1 + \frac{\rho q_m b}{n_e (1 + b C)} \right) \frac{\partial C}{\partial t} = D^* \frac{\partial^2 C}{\partial x^2} \quad (5)$$

The test device in this paper is a test device for diffusion only, the initial and boundary conditions are

$$C(x > 0; t = 0) = 0 \quad (6a)$$

$$C(x = 0; t = 0) = C_0 \quad (6b)$$

$$C(x = L; t > 0) = 0 \quad (6c)$$

Eq.(6a) means that the soil sample is free of contaminant at the initial time ($t = 0$); Eq.(6b) means that the initial source concentration is a constant C_0 ; Eq.(6c) means that the contaminant concentration at the exit of the soil barrier is zero because of the presence of large amount of water.

$$C(0, t) = C_0 - A t \quad (7)$$

where A is a reduction factor.

The contaminant source concentration is reduced nearly linearly with time to account for transfer into the soil barrier.

The contaminant transport through the soil samples was analyzed using Eqs.(5)—(7). These equations were solved by a specially developed FORTRAN 95-based finite difference program. The central difference scheme was used. Some parameters used in this program are listed in Tab.2. The values of isotherm parameters b and q_m were obtained from batch tests as shown in Tab.3.

Tab.2 Parameters used in finite difference program

Parameter	Value
Initial time step/d	0.01
Time step multiplier	1.2
Maximum time step/d	0.5
Minimum time step/d	0.01
Time step reduction factor	0.1
Spacing between grid lines/cm	0.1

Tab.3 The values of b and q_m at different pH values and temperatures

pH	$T = 295\text{ K}$			$T = 313\text{ K}$			$T = 323\text{ K}$			$T = 333\text{ K}$		
	$b / (\text{L}\cdot\text{mg}^{-1})$	$q_m / (\text{mg}\cdot\text{kg}^{-1})$	R^2	$b / (\text{L}\cdot\text{mg}^{-1})$	$q_m / (\text{mg}\cdot\text{kg}^{-1})$	R^2	$b / (\text{L}\cdot\text{mg}^{-1})$	$q_m / (\text{mg}\cdot\text{kg}^{-1})$	R^2	$b / (\text{L}\cdot\text{mg}^{-1})$	$q_m / (\text{mg}\cdot\text{kg}^{-1})$	R^2
5	0.019 2	284.4	0.972	—	—	—	—	—	—	—	—	—
6	0.016 8	261.2	0.974	—	—	—	—	—	—	—	—	—
7	0.014 1	207.6	0.981	0.016 5	260.9	0.985	0.017 5	271.6	0.979	0.019 0	284.1	0.973
9	0.013 2	190.2	0.988	—	—	—	—	—	—	—	—	—

2 Results and discussion

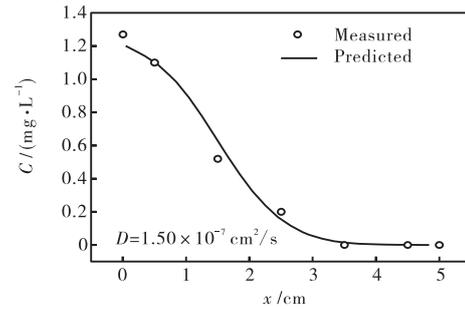
2.1 Diffusion test results

The concentration of source solution is 1.27 mg/L at $t = 1\ 000\ \text{d}$, therefore the value of A in Eq. (7) is found to be 0.061 23. For any given diffusion coefficient D , the concentration at any specified place and time can be obtained by numerical calculation. The values of D were back-calculated by varying D values until the concentration profile predicted by FORTRAN program fit the experimental data well. The concentrations of Cr(VI) in the pore water of the soil versus x at different depths in the soil are shown in Fig.3, where C is contaminant concentration, T is temperature and t is time.

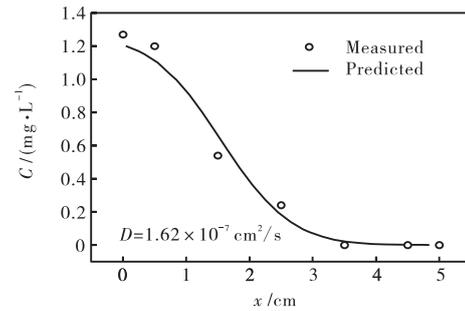
Fig.3 shows that the predicted concentration profiles of that Cr(VI) well fit the observed ones. After a standing time of 1 000 d, the concentration of source solution decreases from 62.5 mg/L to 1.27 mg/L. Some ions may be adsorbed by soil. The concentrations at $x = 3.5\ \text{cm}$ and the exit are both zero, which means Cr(VI) did not break through 5 cm soil sample after a standing time of 1 000 d. The diffusion distance is only 3.5 cm. The diffusion coefficients of Cr(VI) are basically consistent at three different depths, which are $1.50 \times 10^{-7}\ \text{cm}^2/\text{s}$, $1.62 \times 10^{-7}\ \text{cm}^2/\text{s}$ and $2.08 \times 10^{-7}\ \text{cm}^2/\text{s}$ from top to bottom of the test device. The diffusion coefficient on the bottom is a little higher, which may be caused by a higher concentration on the bottom. It is shown in Fig.3 that at the interface between the source and soil sample, there is a sudden change of concentration. This phenomenon agrees with the testing results of Xi *et al.*^[12] and indicates that there is some kind of chemical reaction at the interface. The same phenomenon was found in laboratory and field tests abroad, which needs to be further studied.

2.2 Analysis of influencing factor

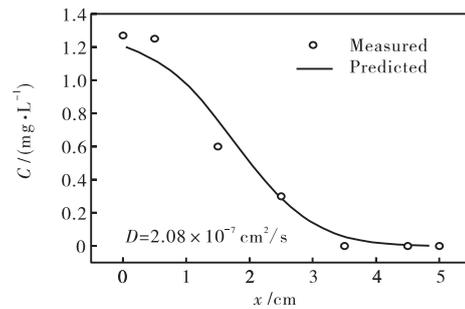
Diffusion coefficient of contaminant in soil can be affected by many factors, such as dry density, temperature, pH value and standing time. In this study the cou-



(a) $z = 2.5\ \text{cm}$



(b) $z = 5.0\ \text{cm}$



(c) $z = 7.5\ \text{cm}$

Fig.3 Measured and predicted concentration of Cr(VI) versus x at different depths

($T = 295\ \text{K}$, $t = 1\ 000\ \text{d}$, $\text{pH} = 7$, $\rho = 1.72\ \text{g}/\text{cm}^3$)

pling effect was not considered. While one parameter changed, the other parameters kept constant. Under the assumption that the concentration of source solution was constant (1.2 mg/L) and diffusion coefficient was $1.62 \times 10^{-7}\ \text{cm}^2/\text{s}$, the influence of each factor on diffusion was calculated. The values of b and q_m at different temperatures and pH values are listed in Tab.3. The results

are shown in Fig.4—Fig.7.

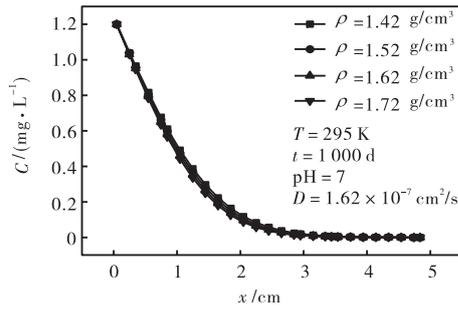


Fig.4 Concentration of Cr(VI) versus x at different dry densities

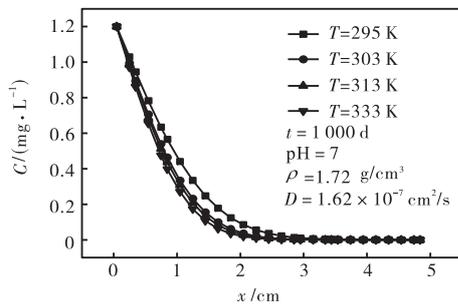


Fig.5 Concentration of Cr(VI) versus x at different temperatures

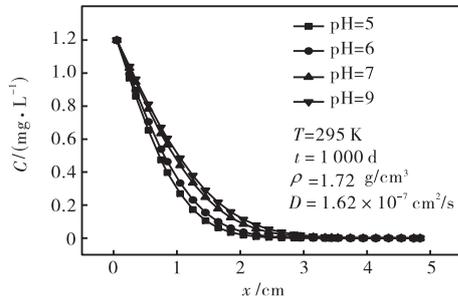


Fig.6 Concentration of Cr(VI) versus x at different pH values

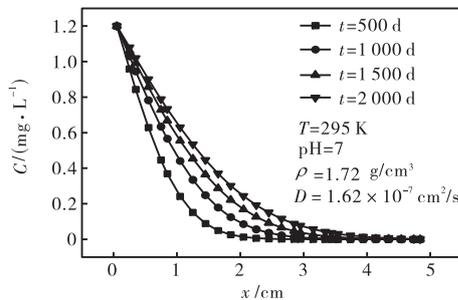


Fig.7 Concentration of Cr(VI) versus x at different time

2.2.1 The effect of dry density on diffusion

The calculation results fit well with the test data done by Xi et al^[15], i.e., diffusion decreases as the dry

density increases. The effect of dry density is mainly on geometric condition. Diffusion meander ratio increases as dry density does. It is shown in Fig.4 that the concentration of contaminant decreases as dry density increases at the same place, temperature, pH value and time. When dry density increases from 1.42 g/cm³ to 1.72 g/cm³, the concentration of contaminant at x = 1.5 cm decreases from 0.298 mg/L to 0.248 mg/L. Diffusion can be reduced by increasing soil dry density.

2.2.2 The effect of temperature on diffusion

Fig.5 shows the diffusion results of Cr(VI) ion in clay soil at different temperatures. It can be seen that the concentration of contaminant in porous water decreases as temperature rises, because when diffusion coefficient is constant, the adsorption of Cr(VI) onto soil increases with temperature. When temperature rises from 295 K to 333 K, the concentration of contaminant at x = 1.5 cm decreases from 0.246 mg/L to 0.107 mg/L.

2.2.3 The effect of pH on diffusion

It is shown in Fig.6 that diffusion distance increases as pH value rises. When pH value is 5, 6, 7 and 9, the concentration of contaminant at x = 1.5 cm is 0.108 mg/L, 0.155 mg/L, 0.248 mg/L and 0.290 mg/L respectively. It can be seen that the initial pH value of the solution has a significant influence on the adsorption of Cr(VI) onto soil. When pH rises, the amount of Cr(VI) adsorbed onto soil decreases, and the concentration of the solution becomes larger. The influence of pH value is stronger in acid environment than in alkaline one. This phenomenon may be interpreted as the adsorption of Cr(VI) onto soil is related to the number of net negative charges in the solution.

2.2.4 The effect of standing time on diffusion

It is shown in Fig.7 that diffusion distance increases with time. The growth rate of diffusion decreases gradually with the same increase amplitude of time. When standing time increases from 500 d to 2000 d, diffusion distance increases from 2 cm to 4 cm and the concentration of contaminant at x = 1.5 cm increases from 0.0899 mg/L to 0.4470 mg/L, which has a breakthrough trend. The effect of time is more significant compared with other factors.

3 Conclusions

This paper describes a number of laboratory tests involving the diffusion migration of Cr(VI) ion through Dalian red clay samples. Back-calculation of diffusion

coefficient of Cr(VI) was made using a specially developed finite difference program. Parametric analysis was conducted to simulate variations in soil dry density, temperature, pH and standing time. The following conclusions are drawn.

(1) The diffusion test device used in this paper is simple and useful, and diffusion progress of contaminant through soil can be easily analyzed.

(2) The concentration of source solution decreases with time. Some ions diffuse into porous water, and others may be adsorbed by soil.

(3) The diffusion coefficient of Cr(VI) in Dalian red clay varies from 1.50×10^{-7} cm²/s to 2.08×10^{-7} cm²/s. After 1 000 d diffusion effect, the concentration of the source solution drops down to 1.27 mg/L from 62.5 mg/L, and the diffusion distance is 3.5 cm.

(4) Under the assumption that diffusion coefficient is constant, the diffusion effect becomes more obvious with lower density, lower temperature, higher pH value, and much more time.

In summary, the method used in this paper to measure the diffusion coefficient of contaminant through soil is feasible, which can provide some reference for theoretical research and practice. However, the size of the model in the test is a little small, and size effect cannot be avoided. If the size can be larger, the result will be more reasonable.

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