

Adsorption and Transport of Heavy Metal Ions in Saturated Soils

by

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Abstract

Laboratory experiments are performed to investigate adsorption and transport characteristics of heavy metal ions in soils. Three divalent cations, lead (Pb^{2+}), copper (Cu^{2+}), and cadmium (Cd^{2+}), which are commonly found in industrial waste, and four different types of soils, loam, bentonite clay, kaolinite clay, and sand, are used. First, batch equilibrium tests are conducted to evaluate the adsorption of the heavy metal ions on each soil and obtain the equilibrium isotherms. Subsequently, column leaching tests are carried out using the same ions and soils to identify the transport mechanism of heavy metal ions through saturated soils. It is revealed that the adsorption of heavy metal ions to soils is in the order loam > bentonite > kaolinite \approx sand, and the selectivity order of heavy metals is $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ for all soils. It is also revealed that the migration of these ions through soil pores is not significantly retarded during the transport process despite the strong adsorption of divalent metal ions on soil particles.

Keywords: Geoenvironmental contamination, Heavy metal ions, Batch equilibrium test, Column leaching test, Adsorption, Transport phenomena

1. Introduction

Heavy metals contaminants are commonly found in several kinds of wastes, including sludge and landfill leachates, and are highly toxic to humans, animals, and aquatic life. The accumulation of heavy metals in soils, their uptake by plants, and the contamination of groundwater with metals including lead (Pb), copper (Cu), cadmium (Cd), nickel (Ni), zinc (Zn), chromium (Cr), and mercury (Hg) have been studied extensively¹⁾.

Concentrations of heavy metals are typically 0-100 ppm in municipal solid wastes and 100-10,000 ppm in sewage sludges, mining wastes, and various industrial wastes, such as those originating from the electroplating, pulp and paper, and chemical industries²⁾. Nevertheless, there is no simple theoretical method for quantitatively predicting the amount of heavy metal ions adsorbed by soils over a period of time.

To study the adsorption characteristics of soils the batch equilibrium test and the soil column leaching test are commonly used. The batch equilibrium test measures the equilibrium adsorption of soil suspensions with various individual contaminants. The entire soil particle surface is exposed to the contaminants and adsorption isotherms are

obtained. Soil column leaching tests examine both the adsorption and the dispersion of contaminants through a saturated soil column. The latter test uses intact soil samples, which have a soil structure, and the adsorption characteristics obtained from this test are the result of the contaminant's interaction with a structured soil system. This method is also used to study contaminant attenuation (migration) profiles resulting from the transport of contaminants through soils.

In this paper, the adsorption of the divalent heavy metal ions, Pb^{2+} , Cu^{2+} and Cd^{2+} , to Kanto loam (a common Japanese volcanic soil), bentonite clay (main component montmorillonite), kaolinite clay (typical clay mineral consisting of silica and alumina sheets), and hill sand are investigated by using batch equilibrium tests. Column leaching tests are carried out using the same ions and sand to examine the ion transport characteristics.

2. Batch Equilibrium Test

Batch tests are conducted with Pb^{2+} , Cu^{2+} and Cd^{2+} , on Kanto loam, hill sand, and bentonite and kaolinite clays. Soils are prepared by air drying, passing through a 2 mm sieve, and grinding to uniform powder. Various initial concentrations of the metal ion solution are used to evaluate the adsorption of metal ions on the suspended soil solids as

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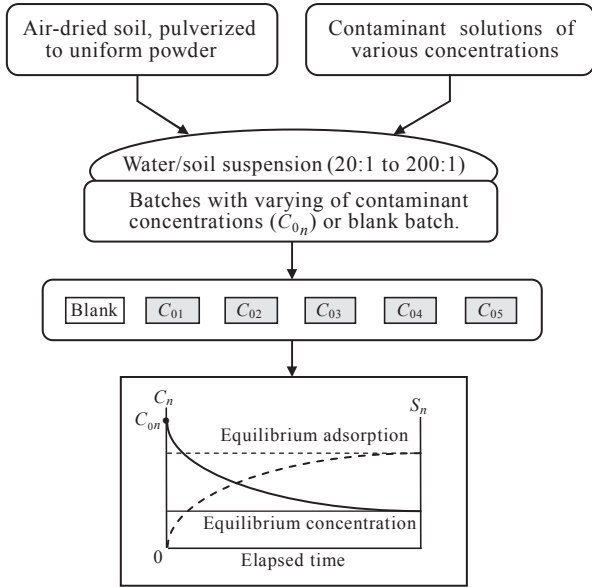


Fig.1 Schematic diagram of batch equilibrium procedure.

the concentration increases. The general procedure for the batch equilibrium tests is shown in Fig.1.

The soil particles must be completely dispersed in this type of experiment. Soil particles (0.5-5.0 g) are added to distilled water (100 mL) (water/soil ratio of 20:1-200:1) and agitated with a magnetic stirrer to produce homogeneous soil suspensions. The change in concentration of the solution with time is measured using an electrochemical ion meter (IOL-40, TOA-DKK) (Fig.2). All tests are carried out at pH=6.

Figure 3 shows the change in ion concentration for the suspensions of Pb²⁺ and Kanto loam. The concentrations gradually decrease because of the adsorption of metal ions on the soil particles. The mass ratio, *S*, of adsorption on soil particles can be calculated for each suspension with



Fig.2 Experimental setup for batch equilibrium test.

$$S = \frac{(C_0 - C)V}{m_s} \quad (1)$$

where *C*₀ is the initial ion concentration of solution (mg/L), *V* is the volume of liquid (mL), and *m_s* is the mass of soil (mg). The numerator in Eq.(1) represents the mass of ions adsorbed onto the soil phase.

Figure 3 shows that equilibrium is achieved for every suspension, from *t* = 20 to 60 min, and as the initial concentration increases the time to reach the equilibrium concentration increases. The values of equilibrium concentration, \bar{C} , and equilibrium adsorption, \bar{S} , are summarized in Table 1. \bar{C} and \bar{S} increase as the initial concentration of the suspension, *C*₀, increases. For Cu²⁺ and Cd²⁺, the equilibrium concentration and adsorption are evaluated using a similar method, and the integrated isotherms are obtained.

The relationships between the equilibrium concentration, \bar{C} , and equilibrium adsorption, \bar{S} , for Pb²⁺ on four different

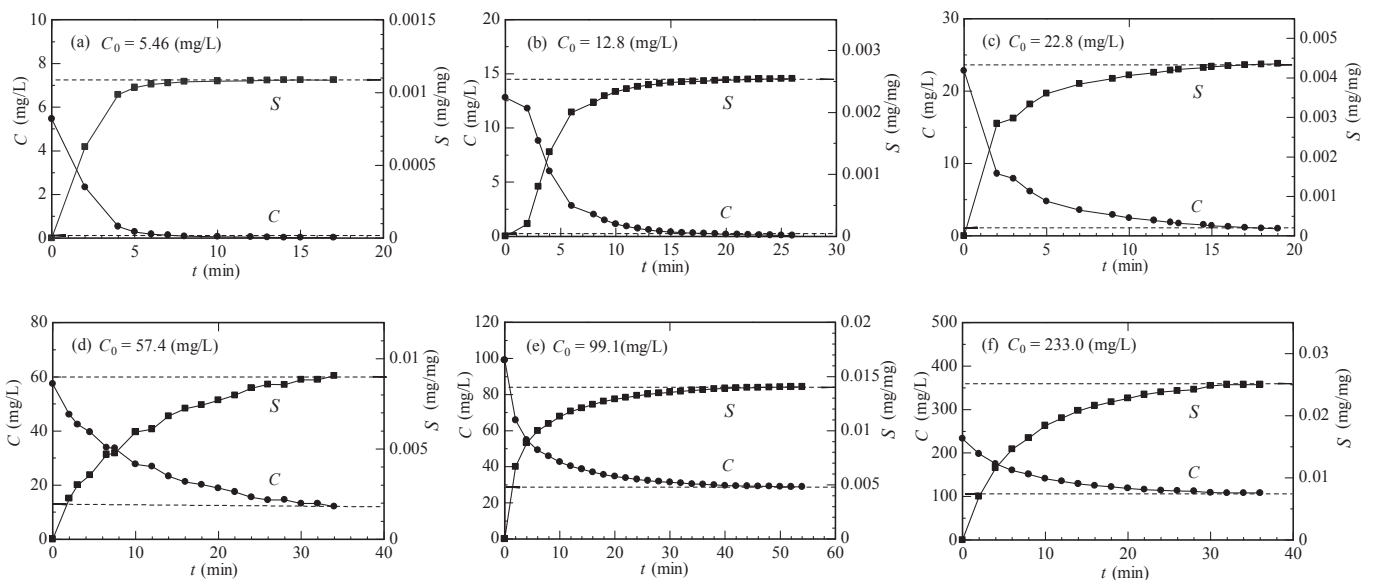


Fig.3 Change in concentration and adsorption in Pb²⁺-loam suspensions.

Table 1 Results of the batch equilibrium tests for Pb²⁺ soil suspensions.

(t*: time to reach equilibrium)

Loam				Bentonite clay				Kaolinite clay				Hill sand			
C ₀ (mg/L)	\bar{C} (mg/L)	\bar{S} (mg/mg)	t* (min)	C ₀ (mg/L)	\bar{C} (mg/L)	\bar{S} (mg/mg)	t* (min)	C ₀ (mg/L)	\bar{C} (mg/L)	\bar{S} (mg/mg)	t* (min)	C ₀ (mg/L)	\bar{C} (mg/L)	\bar{S} (mg/mg)	t* (min)
5.46	0.029	0.0011	18	6.27	1.00	0.0010	51	4.99	3.34	0.0003	15	5.19	4.98	4.2×10 ⁻⁵	80
12.8	0.080	0.0025	26	9.91	1.19	0.0017	120	7.98	5.40	0.0005	12	7.71	7.42	5.8×10 ⁻⁵	60
22.8	1.01	0.0043	19	20.0	4.15	0.0031	120	19.0	13.2	0.0012	12	20.0	19.3	1.4×10 ⁻⁴	66
57.4	12.1	0.0091	34	46.5	21.1	0.0051	102	53.8	39.7	0.0028	8	48.7	46.9	3.6×10 ⁻⁴	62
99.1	28.9	0.0140	50	110.0	54.3	0.0111	102	94.4	77.5	0.0034	16	109.0	106.5	5.0×10 ⁻⁴	70
233.0	108.0	0.0250	32	200.0	144.0	0.0112	108	201.0	183.0	0.0036	8	202.0	197.3	9.4×10 ⁻⁴	70

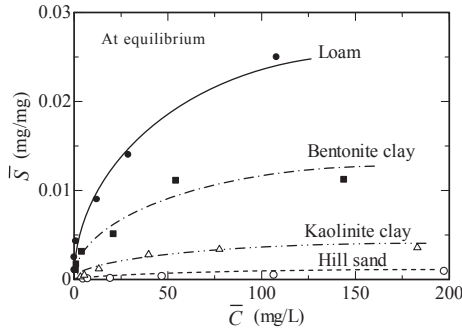


Fig.4 Adsorption of Pb²⁺ on four soils.

soils are shown in Fig.4. The relationships are mostly nonlinear and their functional expressions are given by the following Freundlich equilibrium isotherm

$$\bar{S} = k_1 \bar{C}^{k_2} \tag{2}$$

where k₁ and k₂ are coefficients that depend on the constituents and properties of the soil and mechanism of the interaction with the ion. If the logarithm is taken of both sides of Eq.(2), it becomes

$$\log_{10} \bar{S} = \log_{10} k_1 + k_2 \log_{10} \bar{C} \tag{3}$$

and coefficient k₂ can be determined from the gradient of the straight line of \bar{C} vs. \bar{S} on a double-logarithmic plot³⁾, and k₁ is the \bar{S} -value corresponding to $\bar{C} = 1$.

Figure 5 shows the Freundlich plots of Pb²⁺, Cu²⁺, and Cd²⁺

adsorption on four soils. The adsorption of Pb²⁺ to soils is in the order loam > bentonite > kaolinite > sand, and for Cu²⁺ and Cd²⁺, loam > bentonite > kaolinite ≈ sand.

Selective adsorption of heavy metals occurs when one heavy metal is preferentially adsorbed to a soil. The Freundlich plots in Fig.5 show that the selectivity order of heavy metals is Pb²⁺ > Cu²⁺ > Cd²⁺ for all soils. This agrees with the experimental data reported by Farrah and Pickering (1977), Puls and Bohn (1988), and Biddapa et al. (1981)¹⁾.

The adsorption coefficients obtained from the Freundlich plots are listed in Table2. Coefficient k₁ represents the relative magnitude of adsorption, and k₂ is the degree of nonlinearity between \bar{C} and \bar{S} . The value of k₁ decreases rapidly in the order loam > bentonite > kaolinite > sand, and k₂ is between 0.35 and 0.48 for loam, 0.46 to 0.73 for bentonite, and for kaolinite and sand the values approach 1.

For kaolinite and sand, the isotherms are considered to be linear and expressed as $\bar{S} = K_d \bar{C}$, where the distribution coefficient $K_d \approx k_1$. K_d is a valid representation of the partitioning between liquid and soils if the adsorption that causes the partitioning is fast and small, and only if the isotherm is linear. This may be valid for sand; however, for other soils, heavy metal ions exhibit nonlinear adsorption characteristics. This implies the rate of change of adsorption with concentration is influenced by the concentration in soil pores. Furthermore, the adsorption is also affected by the pH

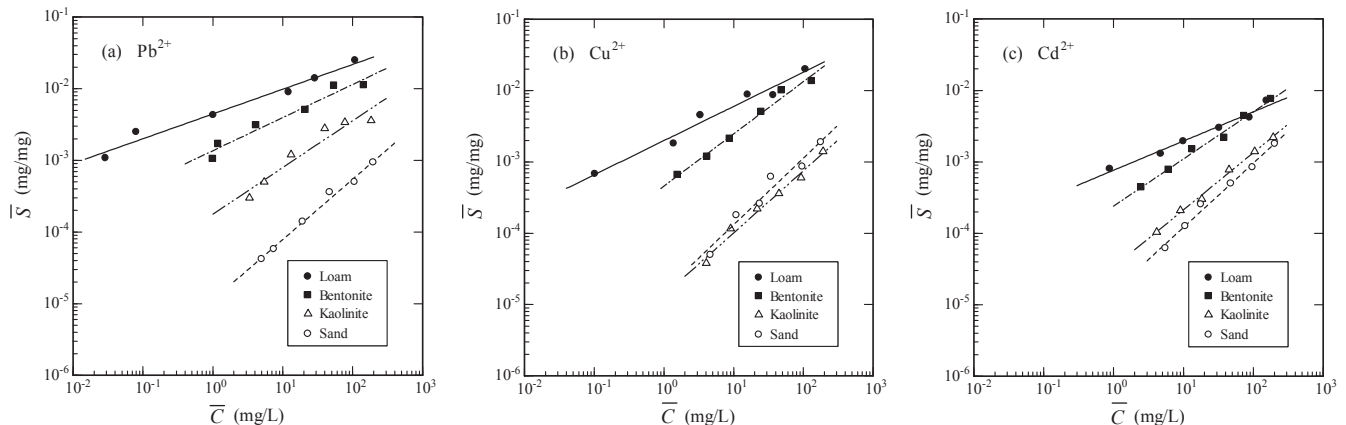


Fig.5 Freundlich plots of equilibrium isotherms of (a) Pb²⁺, (b) Cu²⁺, and (c) Cd²⁺.

Table 2 Coefficients for the Freundlich isotherm.

Ion	Soils	Freundlich Coefficients	
		k_1	k_2
Pb ²⁺	Loam	4.45×10^{-3}	0.345
	Bentonite Clay	1.36×10^{-3}	0.463
	Kaolinite Clay	1.77×10^{-4}	0.652
	Sand	1.13×10^{-5}	0.842
Cu ²⁺	Loam	1.99×10^{-3}	0.479
	Bentonite Clay	4.59×10^{-4}	0.731
	Kaolinite Clay	1.36×10^{-5}	0.871
	Sand	1.53×10^{-5}	0.933
Cd ²⁺	Loam	7.63×10^{-4}	0.409
	Bentonite Clay	2.41×10^{-4}	0.660
	Kaolinite Clay	3.37×10^{-5}	0.800
	Sand	1.54×10^{-5}	0.897

of the solution¹⁾; therefore, all tests were conducted at pH=6.

3. Column Leaching Test

Soil column leaching tests measure the adsorption and diffusion of contaminants through a soil column. Figure 6 shows the method for the column leaching test.

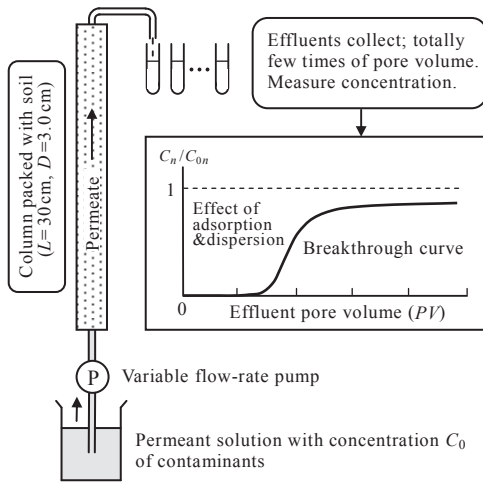


Fig.6 Column leaching test for determining transport characteristics of solute.

A solution of heavy metal ions with a concentration C_0 is pumped up from the bottom of a column at a constant rate. The concentration, C , of the effluent collected from the top of the column is measured over time and the results are plotted as solute breakthrough curves, relative concentration, C/C_0 , versus time, or pore volumes of flow (PV) (Fig.6). PV is the cumulative volume of flow through the soil divided by the volume of the void space in the soil. Expressing total leachate flow in terms of PV is a more convenient method than using elapsed time.

Hill sand was packed in the column and saturated with distilled water. The dry density, ρ_d , is 1.60 g/cm^3 , porosity, n ,

is 0.399, and the volume of void, V_v , is 81.7 cm^3 , which is equal to PV . To determine the degree of dispersion of the solute during the migration, a nonreactive Cl^- solution ($C_0 = 1000 \text{ mg/L}$) is used. Its discharge rate is $q = 0.542 \text{ cm}^3/\text{s}$ and the average flow velocity is $v_{av} = 0.0713 \text{ cm/s}$.

Figure 7 shows the breakthrough curve for Cl^- . The Cl^- ions begin to appear at $V_p \approx 0.9$, and reaches to C_0 after $V_p \approx 1.4$. The gradient of the curve at increasing concentrations represents the degree of dispersion, expressed by the dispersion coefficient, D_L . The pore volume corresponding $C/C_0 = 0.5$ occurred at $V_p = 1$, meaning that the transport of Cl^- is not hindered, because Cl^- does not adsorb to soil particles.

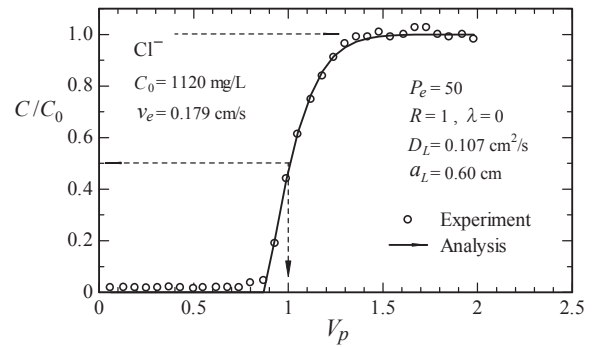


Fig.7 Breakthrough curve for Cl^- -solution.

To determine the adsorption-dispersion characteristics of a soil, the leachate transport through the test soil must be simulated. The one-dimensional transport equation for leachate concentration, C , including retardation and decay caused by adsorption to a soil matrix is expressed as⁴⁾

$$\frac{\partial C}{\partial t} = \frac{D_L}{R} \frac{\partial^2 C}{\partial z^2} - \frac{v_e}{R} \frac{\partial C}{\partial z} - \lambda C \quad (4)$$

where $D_L = a_L v_e$ is the longitudinal dispersion coefficient (cm^2/s), a_L is the dispersivity of soil matrix (cm), v_e is the pore velocity (cm/s), R is the retardation factor, and λ is the decay constant (s^{-1}). The retardation factor R is given for linear adsorption as⁵⁾

$$R = 1 + \frac{\rho_d}{n} K_d \quad (5a)$$

and for non-linear adsorption process as¹⁾

$$R = 1 + \frac{\rho_d}{n} \frac{\partial S}{\partial C} \quad (5b)$$

The analytical solution of Eq. (4) with initial and boundary conditions corresponding to the column leaching test is given by⁴⁾

$$C(L,t) = \frac{C_0}{2} \exp\left(\frac{L}{2a_L}\right) \left\{ \exp\left(\frac{-L\gamma}{2a_L}\right) \text{erfc}\left(\frac{L - v_e t \gamma / R}{2\sqrt{a_L v_e t / R}}\right) + \exp\left(\frac{L\gamma}{2a_L}\right) \text{erfc}\left(\frac{L + v_e t \gamma / R}{2\sqrt{a_L v_e t / R}}\right) \right\} \quad (6)$$

where $\gamma = \sqrt{1 + 4\lambda a_L R / v_e}$, $erfc$ is the complementary error function calculated by using

$$erfc(\beta) = 1 - erf(\beta) = 1 - 2/\sqrt{\pi} \int_0^\beta e^{-x^2} dx \quad (7)$$

Introducing the Péclet number, defined as $P_e = L/a_L$, and effluent pore volume, $V_p (=PV) = v_e t/L$, Eq. (6) can be approximated for large Péclet numbers ($P_e > 10$) as⁶⁾

$$\frac{C}{C_0} = \frac{1}{2} \exp\left\{\frac{P_e}{2}(1-\gamma)\right\} erfc\left(\frac{\sqrt{P_e}}{2} \frac{1-V_p \gamma/R}{\sqrt{V_p/R}}\right) \quad (8)$$

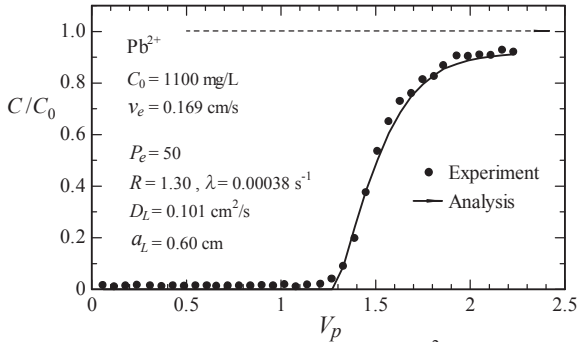


Fig.8 Breakthrough curve for Pb^{2+} -solution.

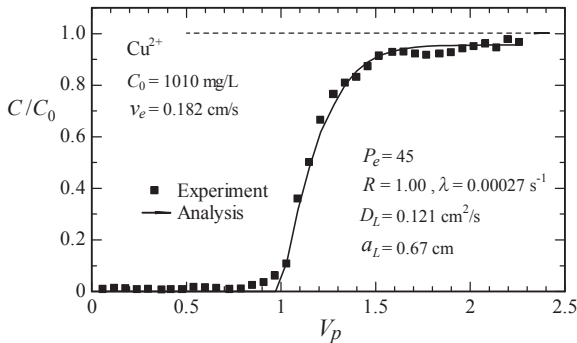


Fig.9 Breakthrough curve for Cu^{2+} -solution.

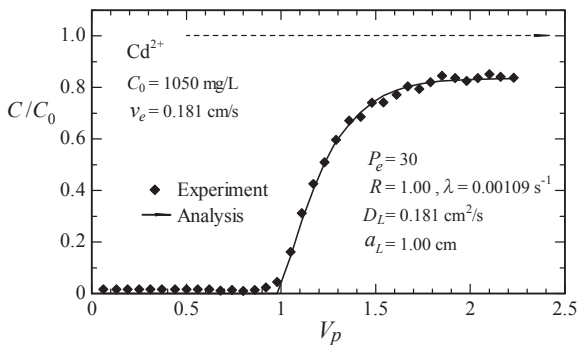


Fig.10 Breakthrough curve for Cd^{2+} -solution.

The best fit curve is found by trial and error, through changing P_e , γ , and R in Eq.(8) to match the experimental results. It is found $D_L = 0.107 \text{ cm}^2/\text{s}$ and $a_L = 0.60 \text{ cm}$ (from $D_L = v_e L/P_e$ and $a_L = D_L/v_e$) (Fig.7).

The results of the column leaching tests for heavy metal ions and their transport analyses are shown in Fig.8-10. The effluent concentrations did not reach C_0 after breakthrough,

because of the adsorption of the ions to the soil. The decay constants were in the range $0.0003 \sim 0.001 \text{ s}^{-1}$, and the highest value is for Cd. The retardation of transport is also observed for Pb^{2+} , where $R = 1.3$. Because the adsorption affects both the retardation and decay of the transport, next we investigate the retardation caused by the adsorption of metal ions to soil by comparing the batch equilibrium test data with the column test data.

4. Transport Mechanism of Heavy Metal Ions Through Soil

Because the adsorption characteristics of heavy metal ions on sand are almost linear (Fig.5 and Table 2), the retardation factor, R , can be calculated using Eq. (5a). To evaluate R , we must treat the units of K_d and ρ_d carefully. If the isotherm is linear, K_d is given by k_1 in the Freundlich coefficient, as described previously, and K_d has units of L/mg because of \bar{S} (mg/mg) and \bar{C} (mg/L). Therefore, the dry density of soil is $\rho_d = 1.6 \text{ g/cm}^3 = 1.6 \times 10^6 \text{ mg/L}$. Using $n = 0.399$ and the distribution coefficients of $K_d = 1.13 \times 10^{-5}$ L/mg for Pb, 1.53×10^{-5} L/mg for Cu, and 1.54×10^{-5} L/mg for Cd, we obtain $R = 46.4$ for Pb, $R = 62.8$ for Cu and $R = 63.2$ for Cd.

These values are high, and inconsistent with the transport retardation observed in the column leaching tests. This is because in the batch equilibrium tests, the entire soil particle surface is exposed to the contaminants, but during the transport in the column leaching tests, contaminants are not directly in contact with the soil particle surfaces and migrate through the center of the voids. Furthermore, the distribution coefficients obtained from batch tests are measured at equilibrium, whereas equilibrium may not be achieved during transport in the column. K_d is valid if the partitioning between the solution and the soil is fast and small; however, it is not valid for transport through soil pores. The discrepancy may be greater for volcanic soil and clayey soils, and we intend to investigate it with further column leaching tests to elucidate the mechanism.

Finally, we discuss the prediction of ground contamination by heavy metal leachate in solid waste landfill. Figure 11 shows a landfill site containing heavy metal ions where the clay barrier that originally protected the side and base has been broken and the leachate has leaked into the sub-ground. The concentration profile for this situation can be calculated using

$$C(z,t) = \frac{C_0}{2} \exp\left(\frac{z}{2a_L}\right) \left\{ \exp\left(\frac{-z\gamma}{2a_L}\right) erfc\left(\frac{z-v_e t\gamma/R}{2\sqrt{a_L v_e t/R}}\right) + \exp\left(\frac{z\gamma}{2a_L}\right) erfc\left(\frac{z+v_e t\gamma/R}{2\sqrt{a_L v_e t/R}}\right) \right\} \quad (9)$$

Figure 11 shows the contamination profile calculated with $C_0 = 1000 \text{ mg/L}$, $v_e = 5 \times 10^{-5} \text{ cm/s}$, $a_L = 0.60 \text{ cm}$, $R = 1.3$, and $\lambda = 1 \times 10^{-7} \text{ s}^{-1}$. As the decay constant due to adsorption increases, the ground contamination becomes more limited close to the surface. Most practical applications require predictions for 25-100 years after construction or completion of the landfill. If data from landfill sites validate our predictions based on laboratory tests, the tests could be used to assess long term geoenvironmental contamination.

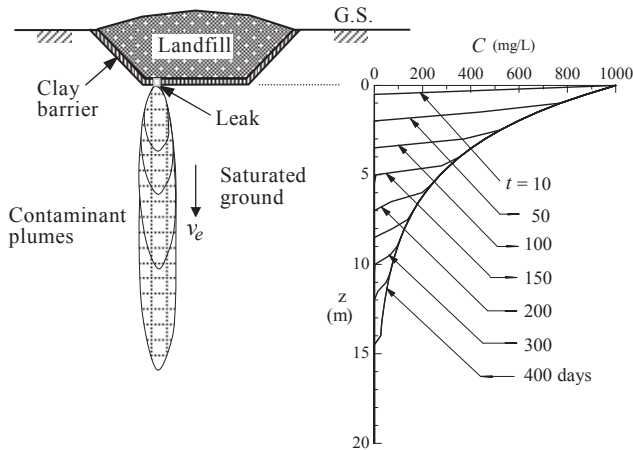


Fig.11 Profile of ground contamination by leachate.

5. Conclusion

Batch equilibrium and column leaching tests are performed to investigate adsorption and transport characteristics of heavy metal ions in soils. The major conclusions from this study are as follows.

1) The amount of adsorption of heavy metal ions (Pb^{2+} , Cu^{2+} , Cd^{2+}) to soils is expressed well by the Freundlich equilibrium isotherm. The relationships between the equilibrium adsorption, \bar{S} , and equilibrium concentration, \bar{C} , are mainly nonlinear for loam, bentonite and kaolinite clays. For sand, the adsorption is nearly linear.

2) The adsorption of heavy metal ions for soils are in the order loam > bentonite > kaolinite \approx sand, and the order of the selectivity of adsorption of heavy metals to soils is $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$. This order is consistent with other published experimental data.

3) Although heavy metals adsorb strongly to soils, the migration of the ions through soils is not significantly retarded. We suggest that there is a different contact and transfer mechanism between ions and soil particle surfaces in the batch equilibrium and column leaching tests. Therefore, it is not appropriate to use retardation factor, R , calculated from the distribution coefficient, K_d , in the batch equilibrium test.

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