

# Some factors controlling diffusive transport of potassium ion through clayey soils

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**Abstract:** To investigate the potential use of two Japanese regional clayey soils, named Ariake clay and Akaboku soil, as soil barrier materials, a series of laboratory diffusion tests are presented. Using an available computer program Pollute V6.3, the effective diffusion coefficients of  $K^+$  of the soils were back-calculated from the diffusion tests. It is found that the Ariake clay has a larger effective diffusion coefficient than the Akaboku soil, indicating that the Ariake clay may provide a better diffusion barrier. A comparison of the effective diffusion coefficients between the single-salt solution condition and the multi-salt solution condition indicates that soils have higher effective diffusion coefficients under the former condition. It is suggested to use miscible solution close to landfill leachates for determining effective diffusion coefficients of specified chemical species for a practical design.

**Key words:** adsorption; Ariake clay; barrier; batch-type test; contaminant; diffusion; landfill

It has been reported that in Japan up to 2000, the remaining available capacity of waste disposal landfill sites is only 3.7 years, which indicates that it is necessary to build more landfills<sup>[1]</sup>. Due to the limited available land in Japan, there is a tendency to build landfills in the coastal area<sup>[2]</sup>, and the local marine clays of interest may provide sources for potential barrier materials. A barrier is usually used to limit the transport of contaminants migrating from the landfill, and minimize the impact of contaminants on the surrounding environment. However, presently in Japan, by far, little has been done to assess the potential utilization of Japanese regional marine clays as barrier materials. In particular, rather little has been published on the study of diffusive transport of contaminants in clays. This results in much uncertainty in the potential application of local marine clays as barrier materials in landfills. Therefore, it is necessary to investigate the diffusive transport of contaminants in regional clayey soils located in Japan.

The purpose of this study is ① to determine the effective diffusion coefficients of potassium ( $K^+$ ) ion of Kyushu regional soils in Japan in order to assess their potential application for barriers in landfill sites, and ② to understand the factors controlling the diffusive transport of  $K^+$  in the soils under the conditions presented in this study.

## 1 Soil Description

Two soils were selected in this study. The two soils are the Ariake clay and Akaboku soil. Specifically, the soils were sampled from Tohoku Town (Ariake clay) and Oomuta City, Fukuoka (Akaboku soil). The Ariake clay is a typical marine sedimentation product that has accumulated in Ariake Bay over the past 10 000 years<sup>[3]</sup>. In the Ariake Bay area, the top 11 m of the Ariake clay sediments have accumulated over 6 000 years under marine conditions. The details of its geological history and depositional geochemistry were provided in Refs. [3, 4], respectively. The detailed origin of the Akaboku soil was discussed in Ref. [5]. Some physico-chemical properties of the soils are shown in Tab. 1.

**Tab. 1** Some physico-chemical properties of the soils

Soil type	Ariake clay	Akaboku soil
Specific gravity	2.62	2.71
Natural water content $w_d/\%$	153	49
Liquid limit $w_L/\%$	116	68
pH at soil: solution (wt. ) = 1:3	8.0	5.5
Clay particle fraction/ $\%$	85	62
Silt particle fraction/ $\%$	14	15
Sand particle fraction/ $\%$	1	23
Primary clay mineral	Smectite	Halloysite
Cation exchange capacity/(meq · (100 g) <sup>-1</sup> )	36.0	11.7

## 2 Materials Preparation

In this study, the synthetic contaminant leachates

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were set as single-salt solution and multi-salt solution. The single-salt solution consisted of potassium chloride (KCl) whereas the multi-salt solution contained potassium chloride (KCl), sodium chloride (NaCl) and calcium chloride ( $\text{CaCl}_2$ ). The Ariake clay and Akaboku soil specimens were prepared by a consolidation process. For the Ariake clay about 502 g in situ soils and for Akaboku soil about 360 g in situ soils were poured into two Plexiglass cylinders with diameters of 60 mm and thicknesses of 151 mm (see Fig. 1), respectively. A porous stone was placed at the base of the soil. Then a vertical consolidation pressure of 3 kPa was applied to the soils. To prevent drying of the soil surfaces and to keep pore fluid close to the original one, about 10 mL pore water extracted from other same soil samples were added on the two soils periodically. After about one month, the load was removed and the specimens were allowed to rebound till finished. The load-unload process lasted for almost a week. Then the cylinders were disassembled and the specimens were quickly cut into 50 mm thick parcels using a thin stainless wire thread in a very careful manner in order to minimize the disturbance to the soil caused by the cut. Water contents of the soils were measured from the cut portions. The cylinder containing source solutions was again connected with the one containing the specimen (see Fig. 1). All of the processes noted above were performed under the laboratory conditions of 25 °C.

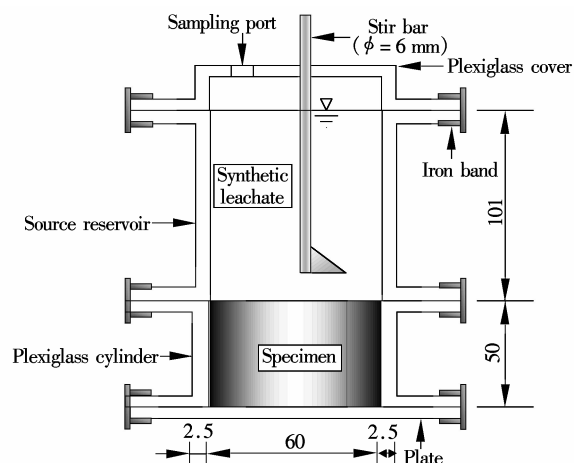


Fig. 1 Schematic of the test apparatus (unit: mm)

### 3 Diffusion Test Method

Prior to the diffusion test, the source solutions were introduced into the source cylinder until the height reached 101 mm. Then the diffusion test was started. A glass stir bar was used to constantly mix the source solutions during the test in order to keep the

concentration of  $\text{K}^+$  homogeneous in the solution. During the test, the concentrations of  $\text{K}^+$  in the source solutions were monitored at two-day intervals by sampling a 0.5 mL solution from the sampling port (see Fig. 1) using a pipetman with a maximum volume of 1 mL. To maintain a constant height of the solutions, the same volume of distilled water was added to the source solution after each sampling. The dilution caused by adding distilled water would be considered by Eq. (3) presented in a later section. The diffusion tests lasted for 14 d for the Ariake clay whereas 6 d for the Akaboku soil. At the end of the test, the solution in the reservoir was removed, and the source reservoir was disassembled. The weight of the soil specimens together with the cylinder were measured and recorded. The specimens were sliced into five sublayers by using a very thin stainless steel thread. For each sublayer, the water content was measured. The whole process was conducted under a laboratory condition maintaining a temperature of 25 °C. The pore fluid concentrations in each sublayer were measured using the method described in Ref. [3]. For each sublayer of the soils, approximately 10 g of the soil was placed into a 500 mL centrifuge tube. Distilled water was added into the tube till the target solid concentration reached 10%. Then the tube was top-sealed, placed into the centrifuge machine and underwent centrifuge at 3 000 r/min. The centrifuge stage lasted for 1 h and finally the supernatant was taken for concentration analysis using the Perkin Elmer Model 3100 atomic absorption spectrophotometer.

## 4 Results and Analysis

### 4.1 Properties of specimens

The properties of the soils and solutions used for the determination of effective diffusion coefficients are shown in Tab. 2. These properties include water content ( $w$ ), degree of saturation ( $S_r$ ), volumetric water content ( $\theta = nS_r$ ), dry density ( $\rho_d$ ), adsorption parameters ( $K_f$  and  $N$ ) and the initial concentration ( $C_0$ ) of  $\text{K}^+$  in the solution. All of the parameters were determined prior to the diffusion test. The water content was determined from the cut portions, and it is assumed that the water content distributes constantly along the soil. Due to the high degree of saturation of soils (see Tab. 2), the difference between total porosity and volumetric water content is quite slight. In this study, volumetric water content was used instead of total porosity in the

numerical analysis. The adsorption parameters ( $K_f$  and  $N$ ) were determined from the batch-type tests by fitting the test result to the Freundlich adsorption equation. The batch-type tests were performed at a 1:4 mass ratio of soil to solution, which is the most recommended ratio by the US EPA Batch-type procedure.

**Tab. 2** Properties of the soils and source solutions

Soil type	Ariake clay		Akaboku soil	
	KCl	Multi-salt	KCl	Multi-salt
Water content $w/\%$	91.9	91.5	70.1	70.1
Dry density $\rho_d/(\text{g}\cdot\text{cm}^{-3})$	0.72	0.71	0.93	0.93
Porosity $n/\%$	70.9	70.9	65.8	65.1
Degree of saturation $S_r/\%$	98.5	98.5	99.0	99.3
Volumetric water content $\theta/\%$	69.8	69.8	65.1	64.6
Thickness of specimen/cm	5	5	5	5
Adsorption parameters	$K_f$	0.077	0.030	0.125
	$N$	0.659	0.735	0.496
Initial concentration of $\text{K}^+$ $C_0/(\text{mg}\cdot\text{L}^{-1})$	960	1 100	1 020	780
Solution collected $q_c/(10^{-10}\text{m}^2\cdot\text{s}^{-1})$ (per area per unit time)	2.5	2.5	2.5	2.5
Height of source solution $H_f/\text{cm}$	10.1	10.1	10.1	10.1
Test period/d	14	14	6	6

## 4.2 Results analysis

The conventional 1-dimensional diffusion equation is used to model the diffusive transport of  $\text{K}^+$  in the soils<sup>[6]</sup>:

$$(\theta + \rho_d K_p) \frac{\partial C}{\partial t} = \theta D_e \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where  $\rho_d$  is the dry density of the soil,  $C$  is the concentration of  $\text{K}^+$  at the point and time of interest,  $t$  is the time,  $x$  is the distance from the chemical source ( $x=0$  represents a plane that is the interface between the source solution and the soils),  $K_p$  is the partition coefficient as expressed in Eq. (2)<sup>[7]</sup>, and  $D_e$  is the effective diffusion coefficient.

$$K_p = \frac{\Delta q}{\Delta C} \bigg|_{C_0} = \frac{q|_{C_0} - q|_{C=0}}{C_0 - 0} = \frac{K_f C_0^N}{C_0} = K_f C_0^{N-1} \quad (2)$$

where  $K_f$  and  $N$  are the adsorption parameters, and  $C_0$  is the initial concentration of  $\text{K}^+$  in the solution.

The upper boundary was imposed by the source solution, which represented a finite mass condition, indicating that the initial concentration of  $\text{K}^+$  would decrease over time. In consideration of conservation of mass, Eq. (3) is used to model the upper boundary:

$$C(t) \big|_{x=0} = C_0 - \frac{1}{H_f} \int_0^t J_f(\tau) d\tau - \frac{q_c}{H_f} \int_0^t C(\tau) d\tau \quad (3)$$

where  $q_c$  is the volume of fluid per unit cross-sectional

area of the soil per unit time removed from the source reservoir,  $H_f$  is the height of the solution in the source reservoir excluding  $q_c$ , and  $J_f$  is the mass flux of  $\text{K}^+$  into the soil underlying the solution, which can be modeled by Fick's First Law as expressed in Eq. (4):

$$J_f(t) = -\theta D_e \left( \frac{\partial C(t)}{\partial x} \right) \quad (4)$$

The lower boundary is imposed by the bottom of the soils, which represents a zero-flux (impermeable) condition, and is modeled by

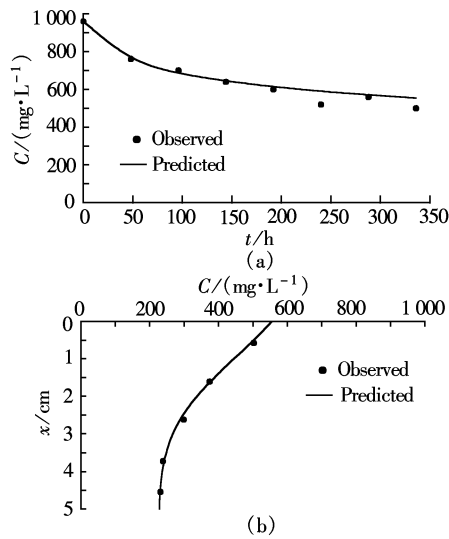
$$\frac{\partial C(t)}{\partial x} \bigg|_{x=L} = 0 \quad (5)$$

where  $L$  is the thickness of the soil.

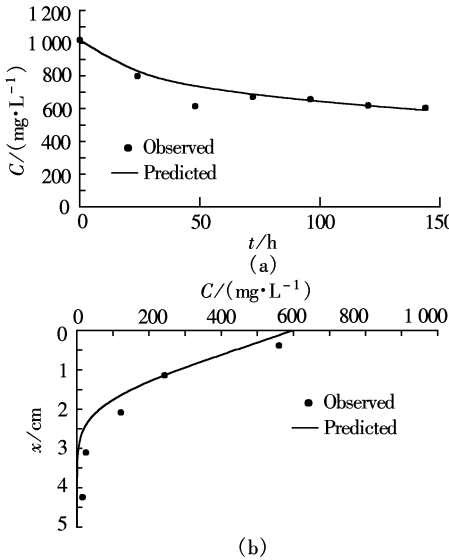
A solution to Eqs. (1) to (5) has been obtained by a semi-analytical and semi-numerical solution, termed "finite-layer technique" developed by Rowe and Booker<sup>[8]</sup>. This solution is done by the following steps: ① simplifying the governing and boundary condition equations by performing the Laplace transform and solving the transformed governing equation analytically, and ② inverting the Laplace transform numerically. A computer program Pollute V6.3<sup>[9]</sup> that incorporates the finite layer technique was used in this study to obtain the solution. Unlike the finite element and finite difference formulations, Pollute V6.3 does not require the use of a "time-marching" procedure, while it can provide numerically accurate results. Pollute V6.3 can also consider the situations where the soils have background (initial) concentrations of chemical species of interest<sup>[10]</sup>. Using Pollute V6.3, theoretically calculated curves for concentration variation with depth in the soils were generated and then compared with the experimental data. The value of  $D_e$ , which gives the best fit "by eye" to the experimental data, was selected as the back-calculated value<sup>[10]</sup>. This value of  $D_e$  was then used to predict the concentration variation with depth in the soil. The input parameters for running Pollute V6.3 are tabulated in Tab. 2. The measured and predicted concentration profiles of  $\text{K}^+$  in the source reservoir and soils are shown in Figs. 2 to 5. It can be seen that the predicted values well fit the experimental ones. The deduced effective diffusion coefficients are listed in Tab. 3.

**Tab. 3** Derived effective diffusion coefficients of  $\text{K}^+$

Soil type	Solution type	$D_e/(10^{-10}\text{m}^2\cdot\text{s}^{-1})$
Akaboku soil	KCl	16.2
	Multi-salt	14.5
Ariake clay	KCl	14.0
	Multi-salt	11.5



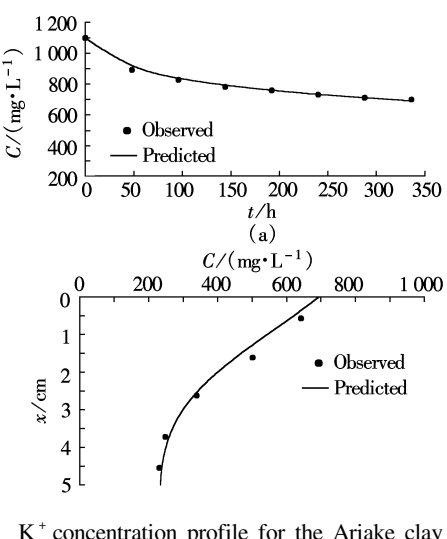
**Fig. 2**  $\text{K}^+$  concentration profile for the Ariake clay in the case of KCl solution. (a) Concentration in the source solution vs. elapsed time; (b) Concentration in the soil vs. depth



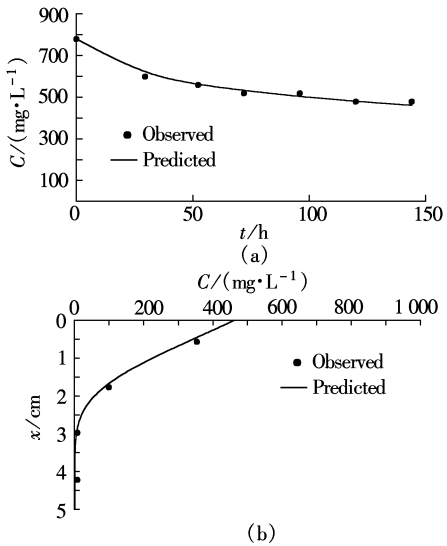
**Fig. 3**  $\text{K}^+$  concentration profile for the Akaboku soil in the case of KCl solution. (a) Concentration in the source solution vs. elapsed time; (b) Concentration in the soil vs. depth

# 5 Discussions

From Tab. 3, it can be seen that under the KCl solution condition, the Ariake clay has a lower effective diffusion coefficient ( $14.0 \times 10^{-10} \text{ m}^2/\text{s}$ ) compared with that of the Akaboku soil ( $16.2 \times 10^{-10} \text{ m}^2/\text{s}$ ). Also, under the multi-salt solution condition, the Ariake clay has a lower effective diffusion coefficient ( $11.5 \times 10^{-10} \text{ m}^2/\text{s}$ ) compared with that of the Akaboku soil ( $14.5 \times 10^{-10} \text{ m}^2/\text{s}$ ), although they were prepared under the same consolidation pressure, 3 kPa. The reason that the Ariake clay has a lower effective diffusion coefficient may be attributed to the more tortuous pore space induced by grain size distribution. As shown in



**Fig. 4**  $\text{K}^+$  concentration profile for the Ariake clay in the case of multi-salt solution. (a) Concentration in the source solution vs. elapsed time; (b) Concentration in the soil vs. depth



**Fig. 5**  $\text{K}^+$  concentration profile for the Akaboku soil in the case of multi-salt solution. (a) Concentration in the source solution vs. elapsed time; (b) Concentration in the soil vs. depth

Tab. 1, the Ariake clay contains a larger amount of clay particles while a lower amount of sand particles than Akaboku soil. The fine particles of the Ariake clay may fill the spaces between the sand particles more effectively, thus possibly leading to smaller pore space and more tortuous pathways for  $\text{K}^+$  to diffuse through the Ariake clay. Therefore, the effective diffusion coefficients of  $\text{K}^+$  for the Ariake clay are lower. The grain size distribution and derived effective diffusion coefficients of the soils are summarized in Tab. 4.

**Tab. 4** Grain size distribution of the soils and effective diffusion coefficients of  $\text{K}^+$

Soil type	Grain size distribution/%			$D_e / (10^{-10} \text{ m}^2 \cdot \text{s}^{-1})$	
	Sand	Silt	Clay	KCl solution	Multi-salt solution
Ariake clay	1	14	85	14.0	11.5
Akaboku soil	23	15	62	16.2	14.5

From Tabs. 3 and 4, it is clear that the effective diffusion coefficient of  $K^+$  obtained from the KCl solution condition is higher than that from the multi-salt solution condition either for the Ariake clay or the Akaboku soil. For the Ariake clay, the effective diffusion coefficient determined from the KCl solution condition is  $14.0 \times 10^{-10} \text{ m}^2/\text{s}$ , whereas that from the multi-salt solution condition is  $11.5 \times 10^{-10} \text{ m}^2/\text{s}$ . The former one is 22% larger than the latter one. For the Akaboku soil, the effective diffusion determined from the KCl solution condition is  $16.2 \times 10^{-10} \text{ m}^2/\text{s}$  whereas that from the multi-salt solution condition is  $14.5 \times 10^{-10} \text{ m}^2/\text{s}$ . The former one is 12% higher than the latter one. These results indicate that for a given soil, the solution compositions would influence the diffusive transport of the specific chemicals, although the other geotechnical conditions (e. g., water content, dry density, porosity, degree and saturation and thickness) remain almost the same. The reasons for the observed phenomena can be explained based on the following geoenvironmental factors.

As indicated in Ref. [11], the diffusion of cations was coupled with the diffusion of anions in order to maintain electro-neutrality. Since  $Cl^-$  ions are non-reactive, they migrated faster in the soil than  $K^+$  ions did. In other words,  $Cl^-$  ions moved ahead of  $K^+$  ions. As a result,  $Cl^-$  ions seemed to need to balance the negative charge from the other in situ cations (which are different from  $K^+$  ions, e. g.  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Na^+$ ) that had been desorbed from the exchangeable sites of soil. Because the concentrations of these desorbed cations in the initial source solution were zero in the KCl solution, the desorbed other in situ cations experienced an upward diffusive driving force which was more significant than that in the multi-salt solution. The upward diffusive driving force tended to reduce the ability of the desorbed cations to migrate downward with the  $Cl^-$  ions. The reduced downward mobility of the desorbed cations in the KCl solution induced a concurrent stronger demand on  $K^+$  ions in the initial source solution to help to balance the negative charges of  $Cl^-$  anions. This, thereby, induced a higher effective diffusion coefficient of  $K^+$  ion in the case of the KCl solution condition than in the case of the multi-salt solution condition.

## 6 Implication to Practice

This study shows that the effective diffusion coefficients of  $K^+$  determined from the KCl solution condition are higher than those determined from the multi-

salt solution condition. As a result, when the effective diffusion coefficients of some key chemical species determined from the condition of single-component solution are used for the design of a soil barrier, the diffusive travel time through the soil barrier will be shorter, while the concentration and mass flux of the contaminant migrating from the bottom of the barrier will be higher, compared with the condition of multiple-component solutions (given that the other conditions remain unchanged). Therefore, the impacts of contaminants on the surrounding ground and the underlying aquifer will be more considerable. To reduce undesirable impacts, an available approach is to build thicker soil barriers in landfills. However, due to the fact that miscible leachate is commonly encountered in landfills, this type of design approach seems to over-estimate the risk, and subsequently provides a cost-ineffective design. As a result, in terms of practice, it is suggested to use miscible contaminant leachates as close to landfill leachates as possible for determining effective diffusion coefficients of specified chemical species for a practical design.

## 7 Conclusions

Several conclusions can be drawn from this study:

- 1) In the case of both the single-salt solution and the multi-salt solution conditions, the deduced effective diffusion coefficients of  $K^+$  for the Ariake clay are lower than that of the Akaboku soil, indicating that the Ariake clay provides a better diffusion barrier material.
- 2) For the two soils, a comparison between the single-salt solution condition and the multi-salt solution condition indicates that effective diffusion coefficients determined from the former case are larger than those determined from the latter case. This solution component-dependent performance implies that for a design of a soil barrier in landfill, using miscible leachates close to landfill leachates may provide a cost-effective design approach.

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## 钾离子在粘性土中扩散运移的影响因素

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**摘要:**为了研究日本九州地区的2种区域性土——有明粘土和赤土作为废弃物填埋场底部粘土衬垫层的适应性,做了一系列室内扩散试验.应用软件 Pollute V6.3 模拟计算了实验结果,反算出了钾离子的扩散系数.研究表明,有明粘土的扩散系数比赤土的扩散系数小,说明有明粘土有望能作为更合适的粘土衬垫材料.通过对比试验研究,发现在混合溶液的情况下,钾离子的扩散系数较在单一溶液的钾离子的扩散系数小.因此建议尽可能使用与现场淋滤液成分相近的混合溶液来做扩散试验,以求出扩散系数来作为废弃物填埋场的设计和性能评估参数.

**关键词:**吸附;有明粘土;粘土衬垫;批处理试验;污染物;扩散;废弃物填埋场

**中图分类号:**V443;X50