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CONTAMINANT ADSORPTION CHARACTERISTICS OF KYUSHU REGIONAL SOILS

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ABSTRACT: Four types of Kyushu regional soils, Ariake clay, Haido, Akaboku, and Diatom earth were selected to evaluate their capacities of contaminant adsorption. The contaminants presented in this study are three types of single-salt solutions, KCl, NaCl and $CaCl_2$ respectively. A batch-type test was performed for each soil and the Freundlich model was adopted to plot adsorption isotherms. It was found that among the tested soils, Ariake clay has the highest adsorption capacity in the case of K^+ and Ca^{2+} ions, whereas Diatom earth fails to adsorb any cation. Based on the adsorption isotherms, the cation selectivity of each soil was given. It is concluded that the contaminant adsorption capacity of clay soil is significantly affected by the soil cation exchange capacity (CEC). For a given soil, it seems that the mobility of the cation of the interested species when it transports through soil is mainly controlled by the cation replaceability, its initially adsorbed concentration and nature of the soil, provided that the other conditions remain constant.

INTRODUCTION

Clay barriers (including natural clay and compacted clay liner) or clay barriers combined with geomembranes in waste disposal landfill are generally used to control the migration of waste leachate in North America and Europe (Rowe, et al. 1995). The most suitable types of clays for clay barriers are those that possess high cation exchange capacity (CEC), large specific surface area, and the presence of surface functional groups that interact with organic and inorganic ions, which exists in waste leachates (Yong et al. 1992). One of the waste retention mechanisms is contaminant adsorption by clay soil barriers. To study the adsorption characteristics of the clay soil, two experimental methods are commonly used in the laboratory: (1) batch-type test (or batch-equilibrium test), and (2) soil column leaching test. The former test provides a quick and easy to perform method through which the soil adsorption isotherm can be obtained and applied to the soil suspensions. The latter test represents a more realistic situation because of the "intact" soil sample instead of the dispersed sample used in the batch-type test. However, this kind of test takes a relatively longer time, and is more restricted to the experiment apparatus. Considering these limitations, in this study, the batch-type test is used to investigate the contaminant adsorption capacities of Kyushu regional soils for their potential use as an engineered soil barrier in waste disposal landfill.

SOIL DESCRIPTION

To complete the objective, four types of soils were selected, locally known as Ariake clay,

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Haido soil, Akaboku soil and Diatom earth in the Kyushu area of Japan. These soils are located at Kohoku Town, Saga (Ariake clay), Oomuta City, Fukuoka (Haido and Akaboku), and Kokonoe Town (Diatom-earth) respectively (Fig. 1). Their physico-chemical properties are shown in Table 1. The cation exchange capacity and exchange cation concentration were measured using the Schollenberger method (Schollengerger and Simon, 1945). To determine the clay mineral composition, moist soil samples were treated with 7% H_2O_2 to remove organic matter, followed by deflocculation by adjusting pH at 10 with 1 M NaOH after sonification. The $<2\mu m$ clay fractions were collected by repeated sonification-sedimentation-siphoning. For X-ray diffraction (XRD), duplicate clay suspensions containing 50 mg clay were prepared. One was washed with 0.5 M $MgCl_2$, the other was washed with 1.0 M KCl, followed by washing with distilled water to move excess salt. 1 cm^3 of water was added and an aliquot of the suspension containing 30 mg of clay was dropped onto a glass slide, air-dried and x-rayed. The K-saturated specimen was heated at 550°C, and the Mg-saturated specimen was solvated with glycerol, followed by X-raying. Filted $CoK\alpha$ radiation from a Rigaku diffractometer was used for the XRD. The percentage of the respective clay minerals in clay fractions were estimated based on the peak areas of the clay minerals in the X-ray diffraction patterns (Wada, 1966).

Fig. 1 A sketch map of soil sampling locations in the Kyushu region of Japan

MATERIALS PREPARATION

Soil Sample

To perform the test, each type of soil was spread out on a flat surface no more than 3cm deep, and allowed to air dry for 7~10 days until constant weight (a change was less than 5% during 24 hours period) was achieved. After the sample had air dried, it was passed through a 2-mm screen sieve. Large aggregates were crushed without grinding using a rubber-tipped pestle. The sieved soil was mixed to obtain uniformity, and the water content was measured by taking two portions of the soil and placing them into an oven under 110°C for at least 24 hours and recorded.

Table 1 Physico-chemical properties of the tested soils

Soil type	Ariake clay	Haido	Akaboku	Diatom earth
Specific gravity	2.62	2.66	2.71	2.14
Natural water content, w_n (%)	153	52	48.8	165
Liquid limit, w_L (%)	116	67	68	—
Plastic index, I_p	65.5	9.2	27.1	—
pH at 1:3 soil:solution	8.0	5.9	5.5	2.5
Clay particle content (<0.005mm) (%)	85	63	62	20
Clay mineral content (%)				
Smectite	40	—	—	—
Illite	34	—	—	—
Kaolinite	22	—	—	—
Vermiculite	4	—	—	—
Halloysite	—	49	100	—
Metahalloysite	—	51	—	—
Cation exchange capacity (meq/100 dry soil)	36.0	11.8	11.7	8.09
Exchangeable cation concentration (meq/100 g dry soil)				
Na^+	14.4	0.34	0.19	0.31
Ca^{2+}	7.49	3.60	5.18	4.53
K^+	4.05	2.04	0.38	0.77
Mg^{2+}	12.6	1.06	0.72	1.49
Pore fluid concentration (meq/L pore water)				
Na^+	42.3	1.27	0.80	1.03
Ca^{2+}	8.48	1.86	3.40	2.46
K^+	8.03	0.32	0.03	0.26
Mg^{2+}	33.7	0.86	0.88	1.40
HCO_3^-	20	ND<1	ND<1	ND<1

Contaminant Leachate

In this study, three kinds of single-salt synthetic contaminant leachates (KCl, NaCl and $CaCl_2$ solutions) with a set of different targeted initial concentrations were adopted respectively. They were selected since (1) they are major constituents in most MSW landfill leachates (Wigh 1979; Griffin and Shrimp 1978, and Rowe et al. 1995); (2) they are easy to be dealed with because of their very low toxicity in terms of human health, and (3) Both of K^+ and Na^+ have lower replaceability relative to heavy metal when transport through soils with montmorillonite, illite and kaolinite clay minerals (Triegel 1980 and Mehlich 1981). Hence each of them seems to represent a "trace cation". The typical replaceability of the selected cations is show in Table 2.

Table 2 Typical replaceability of the selected cations (after Triegel 1980 and Mehlich 1981)

Soil type	Replaceability
Montmorillonite	$Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > H^+ > K^+ > Na^+$
Illite	$Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > H^+ > K^+ > Na^+$
Kaolinite	$Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > H^+ > K^+ > Na^+$

TEST METHOD

The batch test consists of placing 10 g (oven-dried basis) of prepared soil sample together with 200 mL single-salted synthetic leachate into a 250 mL Erlenmeyer flask. Then the flask was top sealed and placed in an end-over-end rotary mixer, and shaken at 29 rpm for 24 hours. At the end of the mixing period, a sample of the soil-solution slurry from the flask was poured into a 50-mL centrifuge tube, sealed with cap, and placed in a centrifuge. The tube was centrifuged for 20 minutes at 3000 rpm. After that, the supernatant from the tube was pipetted into a sample bottle. All of the procedures mentioned above were conducted at the temperature of 25°C. Finally the concentration of the specified cation in the sample bottle, titled equilibrium concentration was measured using HITACHI Z-6000 atomic adsorption spectrophotometer. The procedure was repeated until each soil was completed.

The results of the chemical analyses were plotted in the form of adsorption isotherm, or equilibrium concentration, C, versus sorbed concentration, q, of solute species. The sorbed concentration, q, was determined using the following equation:

$$q = \frac{(C_o - C)V_{sol}}{M_s} \tag{1}$$

where C_o is the initial concentration of the specified cation in the flask, C is the equilibrium concentration, V_{sol} is the volume of the solution (200-mL in this case) and M_s is the soil mass (10 grams in this case).

RESULTS AND DISCUSSIONS

Several adsorption isotherm equations have been used to predict relationship between the sorbed and equilibrium concentrations resulting from the batch test. Many of these equations are covered by Kinniburgh (1986). Current available models for adsorption isotherms are (Yong et al. 1992):

(1) Freundlich model, which is expressed as:

$$q = K_f C^n \tag{2}$$

where K_f and n are the parameters adjusted to fit the Freundlich equation to the experimental data. In the case of $n=1$, it represents a Constant model.

(2) Langmuir model, which is given as:

$$q = \frac{K_L M C}{1 + K_L C} \tag{3}$$

in which K_L and M are the corresponding parameters, and can be obtained through fitting the equation to the experimental data.

Since the isotherms presented in the paper show no linear profile, the constant model is not taken into consideration. The calculated parameters for the Freundlich model and the Langmuir model are shown in Table 3.

Table 3 Adsorption isotherm parameters of the tested soils

Parameter	Ariake clay			Haido			Akaboku		
	K^+	Na^+	Ca^{2+}	K^+	Na^+	Ca^{2+}	K^+	Na^+	Ca^{2+}
				Freundlich model					
K_f	0.077	—	0.855	0.126	0.158	0.037	0.240	0.567	0.019
n	0.659	—	0.222	0.475	0.231	0.494	0.380	0.126	0.534
r	0.998	—	0.829	0.934	0.491	0.902	0.741	0.387	0.600
$RMSE$	0.124	—	0.529	0.353	0.225	0.152	0.777	0.371	0.397
				Langmuir model					
K_L	0.015	—	0.075	0.020	0.008	0.003	0.071	0.251	0.002
M	0.001	—	0.019	0.006	0.010	0.002	0.029	0.203	0.002
r	0.996	—	0.919	0.953	0.525	0.962	0.556	0.108	0.618
$RMSE$	0.282	—	0.383	0.556	0.218	0.154	1.000	0.395	0.269

To compare the two types of models, the Root Mean Square Error, $RMSE$, is adopted. Combined with the Correlationship Coefficient, r. $RMSE$ is written as:

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n} d_i^{\,2}} \tag{4}$$

in which d_i is the difference between the model predicted and the measured value of the sorbed concentration from the batch-type test. n is the number of measured values. The values of $RMSE$ and r are shown in Table 3. From Table 3, it can be seen that in terms of r, the fitness of the Langmuir model to the experimental data is slightly better than that of the Freundlich model for Haido because of the small difference of the r values between these two models, whereas it is worse than that of Freundlich model for Akaboku. In terms of $RMSE$, five of the eight cases (Table 3) show lower *RMSE* values in the Freundlich model than in the Langmuir model, indicating that the Freundlich model fits better to the experimental results than the Langmuir model. Thus, it may be concluded that given the soils and range of contaminant concentrations covered in this study, the Freundlich model fits better to the experimental data. Also, the conventional EPA (1985) standard suggests that the Freundlich isotherm equation is used more frequently due to its ease of application. On the basis of the two reasons mentioned above, the Freundlich model, therefore, is adopted for this study.

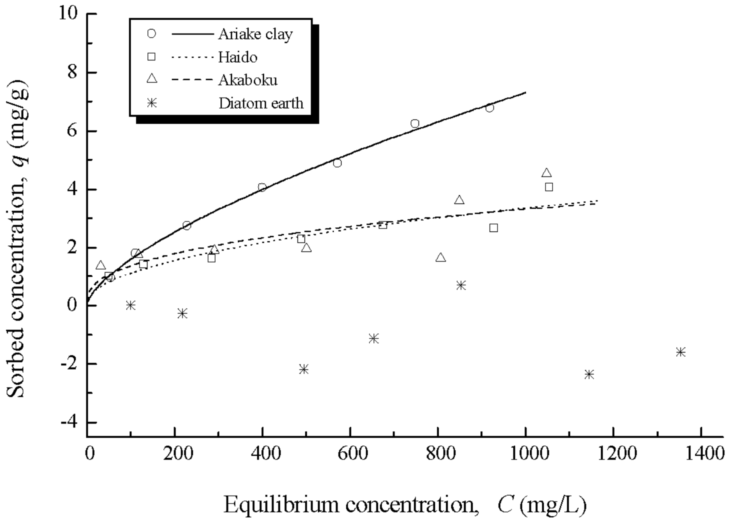

Fig. 2 Freundlich model-fitted K^+ adsorption isotherm of the tested soils

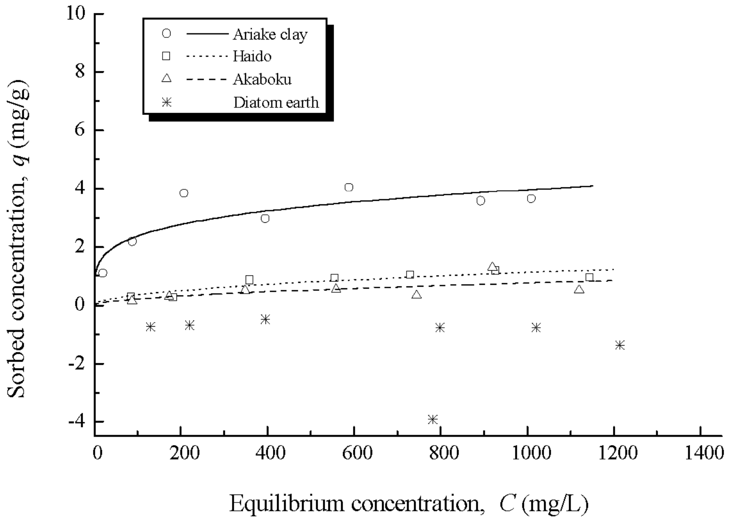

Fig. 3 Freundlich model-fitted Ca^{2+} adsorption isotherm of the tested soils

To compare the adsorption ability of the investigated soils, the Freundlich-fitted cations adsorption isotherms were plotted for each of the tested soils. It is clear that the Ariake clay has the largest adsorption capacity in the case of K^+ (Fig. 2) and Ca^{2+} (Fig. 3). It adsorbs these two types of cations at almost three times the rate of Haido and Akaboku (Figs. 2 and 3). To a large degree, this is due to the higher cation exchangeable capacity (CEC) of Ariake clay relative to the other tested soils. Its CEC value, 36.0 is about three times as large as those of Haido and Akaboku, which are 11.8 and 11.7 respectively (Table 1). On the contrary, in the case of Diatom earth for the three types of chemical species, the sorbed concentration, *q*, appears as a minus value (Figs. 2 to 4), indicating they are not operative to be adsorbed. This is mainly because of its lower, clay particle content and pH value (Table 1). Yong et al. (1992) and Mitchell (1992) showed that low clay particle content would result in low soil specific surface area, and consequently led to low adsorption since soil particle specific surface area considerably affected adsorption capacity. Mullins and Sommers (1986) indicated that low pH tended to cause an increase in competition with H^+ at the exchange sites on the soil and thus led to a low adsorption. Pickering (1986) indicated that at a low pH value, most of the exchange sites of soils were occupied by H^+, and H^+ had a high affinity for these sites. Hence these exchange sites tended to refuse adsorbing cations even though their concentrations increased. Initially, it was expected that Na^+ adsorption, as well as K^+ and Ca^{2+} adsorption would be feasible in Ariake clay. However, from the Fig. 4, it can be seen that Na^+ is not adsorbed at all over the given range of concentrations presented in the paper. This is not surprising since the initially adsorbed cations at the Ariake clay soil particle exchange site is dominated by Na^+ (Table 1), of which the concentration is even higher than the maximum one in the set of the designed synthetic leachates. This, therefore, induces the failure of Na^+ adsorption of Ariake clay. Based on the data analysis mentioned above, the cation adsorption ability order of the tested soils is summarized in Table 4. This result is consistent with that provided by Du et al. (1998) using the "simple" batch test, of which the in-situ soil is used instead of the sieved one for performing the batch test.

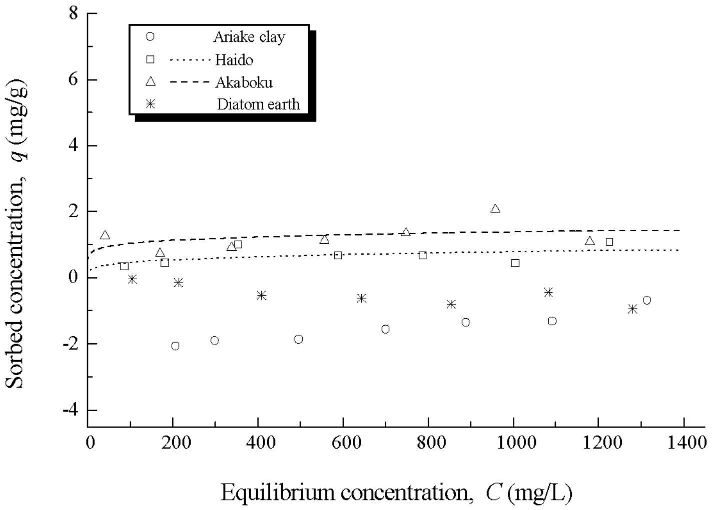

Fig. 4 Freundlich model-fitted Na^+ adsorption isotherm of the tested soils

Table 4 Cation adsorption ability order of the tested soils

Cation species	Adsorption ability order
K^+	Ariake clay > Haido, Akaboku (no significant difference)
Na^+	Haido, Akaboku > Ariake clay, Diatom earth (no adsorption is operative)
Ca^{2+}	Ariake clay > Haido, Akaboku (no significant difference)

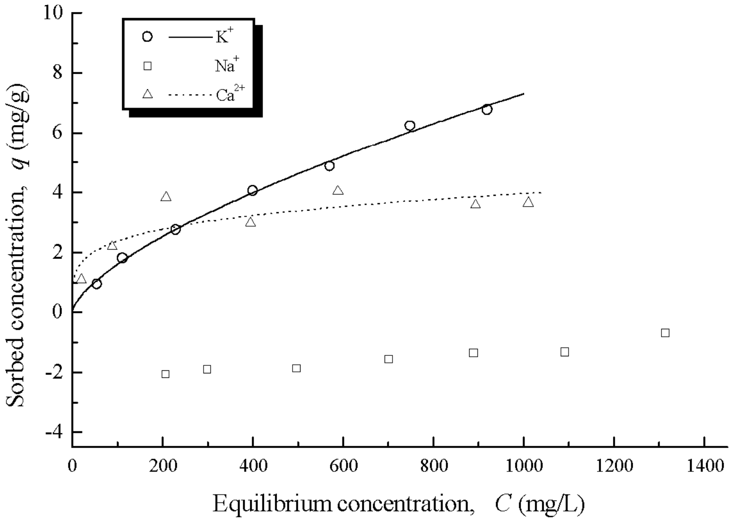

Fig. 5 Freundlich model-fitted cations adsorption isotherm of Ariake clay

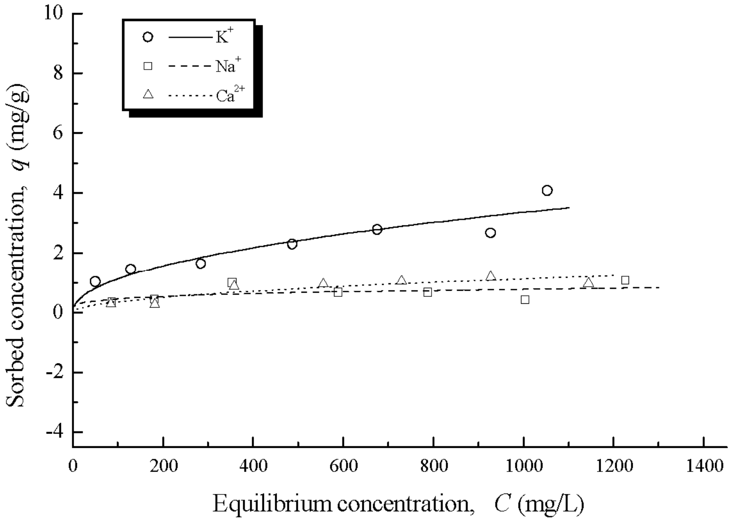

Fig. 6 Freundlich model-fitted cations adsorption isotherm of Haido

Shackelford (1988) studied the replaceability of three types of cations, K^+, Zn^{2+} and Cd^{2+}, for two types of soils through a batch-type test, and provided the cation adsorption selectivity for each tested soil. In order to determine the cation selectivity of the soils used in this study, and insight into the controlling factors, the Freundlich model fitted cation adsorption isotherms of each of the tested soils except for Diatom earth are plotted. It can be seen from these figures that of the three cations of interest, K^+ is the least mobile of the three soils (Figs. 5 to 7), and Ca^{2+} is the most mobile for Haido (Fig. 6, no significant difference between Ca^{2+} and Na^+) and Akaboku (Fig. 7), whereas Na^+ is the most mobile for Ariake clay (Fig. 5). This seems to be inconsistent with the typical cation exchange series shown in the literature study (Mitchell 1992). It may be attributed to the following factors: (1) The literature test was conducted under the controlled conditions (pH and soil: solution ratio, ect.). Since both kaolinite and halloysite have a pH-depent charge, pH control is important for soils containing significant content of kaolinite or halloysite which may result in anion adsorption (Zhang and Zhao 1997). (2) Complexed Ca may exist in the case of $CaCl_2$ solution. While performing the batch test using $CaCl_2$ solution, Ca^{2+} may tend to combine with HCO_3^-, which exists in the pore fluid of Ariake clay (Table 1) and may form as a result of the dissolved CO_2 in the solution, and form into complexed $Ca(HCO_3)^-$ cation. The complexed cation has larger size than K^+ and Na^+, and therefore compete less favorably for the exchange sites (Mitchell 1992). (3) The lower initially adsorbed concentration of K^+ on the soil particle surface relative to that of Ca^{2+}(Table 1, for Ariake clay, Haido and Akaboku). Since at the exchange site the binding energies for metal associated with lower initial adsorption density are larger relative to that with higher initial adsorption density (Reed and Cline 1994), K^+ seems to be more favorably adsorbed. This may also be applied to the case of Akaboku where Ca^{2+} appears to be more mobile than Na^+ (Fig. 7), although its replaceability is higher than that of Na^+ (Mitchell 1992). Also the higher replaceability of K^+ than that of Na^+ (Mitchell 1992) is another reason despite the fact that the initially adsorbed concentration of the former is slightly higher than that of the latter (Table1, for Haido and Akaboku). In the case of Haido, it adsorbs Na^+ and Ca^{2+} without significant difference in amount (Fig. 6), indicating that their mobility does not differ too much. Thus it may be concluded that the cation adsorption characteristics for a given soil is not only controlled by its replaceability, but also by its initially adsorbed concentration at the exchange site of the soil particle surface and nature of the soil, provided that the other conditions remain constant. The cation mobility order of each of the tested soils except for Diatom earth is then summarized in Table 5.

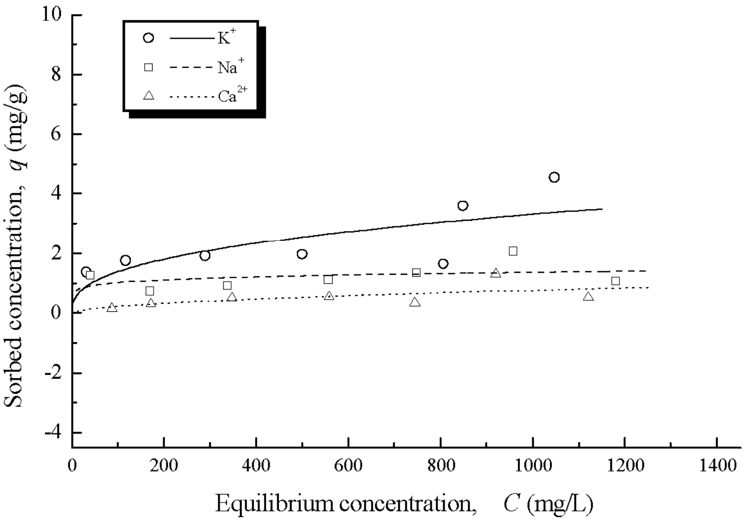

Fig. 7 Freundlich model-fitted cations adsorption isotherm of Akaboku

Table 5 Cation mobility order of the tested soils

Soil type	Cation mobility order
Ariake clay	$Na^+ > Ca^{2+} > K^+$
Haido	Na^+, Ca^{2+} (no significant difference) $> K^+$
Akaboku	$Ca^{2+} > Na^+ > K^+$

CONCLUSIONS

This study aims to investigate the contaminant adsorption properties of four types of Kyushu regional soils by batch-type test according to conventional ASTM (1993) standards. The adsorption isotherms of the tested soils are obtained from the test, and they appear no linear shape.

The failure to determine the clay mineral content of Diatom earth is due to the fact that it is poorly crystalline. The high silt content (65%) of Diatom earth results in the failure of measuring its liquid limit and plastic index.

Of the two physical models which quantitatively describe the relationship between the experimental data and the batch test, the Freundlich model fits better to the experimental data than the Langumir model does, based on the value of *RMSE* and *r*.

The adsorption isotherms indicate that as for the three single-salt synthetic leachates, Ariake clay shows larger adsorption capacity in the case of K^+ and Ca^{2+} than the other tested soils. It adsorbs these two types of cations at almost three times the rate of Haido and Akaboku. This is mainly due to the higher CEC of Ariake clay than those of the other soils, whereas low CEC, clay content and pH value of Diatom earth results the failure of any cation adsorption.

The cation mobility order presented in this paper suggests that for a given soil, the cation adsorption characteristics is not only controlled by its replaceability but also by its initially adsorbed concentration at the exchange site on the soil particle surface and nature of the soil, provided the other conditions remain unchanged. This is well described by the phenomena that K^+ is preferred over other two cations for all of the tested soils except for Diatom earth, and the Na^+ adsorption is not operative in Ariake clay.

It seems that among the tested soils, Ariake clay is the most ideal material for the potential use as a soil barrier in waste disposal landfill. However, further research must be done since the leachate presented in this paper is a single-salt solution instead of a multi-salt one, which is quite common in the waste leachate, and other properties such as diffusion transportation performance also need to be investigated.

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