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A study on heavy metal migration in fly ash/bentonite using a reactive transport model

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Abstract: The retardation of heavy metals in a mixture of fly ash and bentonite was studied as a potential barrier material for a landfill. Column tests were conducted using synthetic leachate having 100 mg/L and 50 mg/L of lead (Pb) and cadmium (Cd), respectively. Results indicated that the mixture had obvious retardation ability for heavy metals. To investigate the retardation factor caused by adsorption, batch adsorption tests were conducted at various concentrations. Test results were correlated with both Langmuir and Freundlich isotherms. The adsorption of the lead ion was applicable to the Langmuir isotherm and the adsorption of the cadmium ion was applicable to the Freundlich isotherm. In addition, based on experimental results, the migration characteristics of heavy metals through the bed of fly ash and bentonite mixture were investigated using the PHREEQC, a reactive transport model, under the real conditions of the landfill liner.

1. Introduction

Landfills have to be designed to minimize adverse effects of waste disposal but many are poorly designed. As a result, leachate containing organic compounds and heavy metals are contaminating ground water and they have the potential to affect human health. Fortunately, various waste management techniques have been developed and the percentage of waste treated by landfills is continuously declining. In the case of Korea, the landfill disposal rate decreased from 86.1% in 1993 to 43.4% in 2001. But the demands on landfills will continue due to the increasing amount of wastes and the present landfill capacity. A modern sanitary landfill requires isolation of waste from the environment. In order to contain leachate securely, an impermeable soil barrier or artificial liner covers the bottom of the landfill. Generally, the lining system is a composite barrier consisting of a flexible membrane liner, over a thick layer of compacted soil having a hydraulic conductivity no greater than 10^{-9} m/s. In most cases, a layer of clay is used. However, it would be highly desirable to use a barrier material that has the ability to not only be an effective hydraulic barrier but to also be a chemical barrier.

There are a number of studies on utilizing fly ash as an alternative landfill barrier material (Edil et al., 1987; Shackelford et al., 1994; Lee at al., 2000). Fly ash is a waste produced from coal-fired power stations. The specific area of fly ash is about 3,000 ㎠/g and it consists mainly of SiO_2 and Al_2O_3. Because of its physical properties and pozzolanic activities, fly ash is widely used in the cement and concrete industry. Fly ash also has a strong alkalinity of pH 10-13 when added to water, and its surface is negatively charged at a high pH. Hence, it has the ability to remove heavy metal ions from aqueous solution by precipitation or electrostatic adsorption (Oh, 2002). Therefore, fly ash has the potential to be a good chemical barrier to restrict the underground migration of heavy metal ions. However, fly ash alone does not give a satisfactory hydraulic conductivity (10^{-5}-10^{-6} m/s); other materials such as bentonite should be used with fly ash to obtain the required hydraulic conductivity.

In this study, the adsorption of heavy metal ions on fly ash/bentonite mixture was investigated through batch and column experiments. Based on the experiment results, the transport profiles of metal ions were simulated by changing the influent concentration, the initial pH, the barrier thickness and the diffusion coefficient. To model a geochemical transport, PHREEQC (Parkhurst and Appelo, 1999) was used. PHREEQC in common use is based on an ion-association aqueous model and can handle speciation, saturation-index calculations, batch-reaction and one-dimensional transport calculations involving reversible and irreversible reactions and inverse modeling.

2. Materials and methods

Materials and Equipments

The fly ash used in this study was obtained from Korea Electric Power Corporation and the activated sodium bentonite was obtained from Korea Sud-Chemie Corporation. The stock solutions of cadmium and lead were made by dissolving the chloride salts $CdCl_2$ and $PbCl_2$ (Junsei Chemical Co., Ltd.) in distilled water. The concentrations of heavy metal ions were analyzed by an atomic absorption spectrometer (PerkinElmer AAnalyst 100) and the concentration of bromine ions was measured by an ion chromatography (DX 500 Chromatography). pH measurements were made using a pH meter (SUNTEX). The size distributions of the fly ash and bentonite samples were analyzed by a modular particle size analyzer (Malvern Mastersizer S).

Tests were conducted using fly ash (Sample 1) and fly ash/bentonite mixtures in a 9:1 mass ratio (Sample 2). The fly ash sample was screened at 200 mesh and the –200 mesh material was used in all experiments. Before the experiments, fly ash was dried at 105℃ for 2 hours and bentonite was dried at 70℃ for one night.

Adsorption tests

For adsorption tests, 0.5 g of the samples were mixed with 25 ml distilled water in 50 ml polyethylene bottles and were hydrated for 8 hours in a shaking incubator at 25℃ to make the pH stable. pH was then adjusted to 6 by adding 1M HCl. The stock solution was injected in to the bottles to make initial concentrations of 5-200 mg/L. The bottles were agitated at the conditions of 25℃ and 130 rpm until equilibrium was obtained. Blank experiments were conducted at the same conditions.

The equilibrium times of each sample and heavy metal were predetermined from kinetic experiments. The experiments were conducted using a procedure similar to the adsorption experiments. The initial concentrations of the cadmium and lead ions were 50 mg/L and 100 mg/L, respectively, and the time intervals were 5-480 minutes.

Column tests

The column used in this study consisted of simple hollow acryl cylindrical cells with an inside diameter of 2 cm and a height of 5 cm. The apparatus had one-directional flow with the feed solution flowing from a reservoir to the column at 1.2 m constant pressure head. The fly ash and fly ash/bentonite samples were packed separately in two columns and were saturated with distilled water until the flow rate stablized. Through performing tracer experiments, seepage velocity and dispersion coefficient were calculated. Bromine ion was used for the tracer and the influent concentration was 10 mg/L. Following the tracer experiments, the heavy metal solutions were placed on the reservoir. The initial concentrations of metal ions were 50 mg/L for cadmium and 100 mg/L for lead. The metal solutions were previously adjusted to a pH of about 3.5-4.0 in order to reduce the experiment period. The leachate was collected at the lower part of the column. The collected solution weight was used to measure a leachate flow rate. To prevent precipitation of soluble species in the collected leachate during storage, solutions were acidified to a pH of less than 1 with 1M HCl.

3. Results

Characteristics of fly ash and bentonite

Table 1 shows the chemical composition of experimental materials. SiO_2 and Al_2O_3 make up about 80 percent of both the fly ash and the bentonite. The LOI (Loss on Ignition) of fly ash is relatively low at 2.93 percent since the +200 mesh material containing high unburned carbon was removed by sieving. The Na_2O content of sodium bentonite is 4.24 percent. Fig. 1 shows the particle size distributions of the fly ash and the bentonite. The average particle sizes (D_{50}) of the bentonite and the fly ash are 7.82 μm, and 30.66 μm, respectively. The fly ash has a narrower distribution; about 3% of the fly ash particles are larger than 100 μm compared to 10% of the bentonite being larger than 100 μm. Again, this is because the +200 mesh material was removed from the fly ash.

Table 1. Chemical composition of fly ash and bentonite.

Sample	Fly ash (%)	Bentonite (%)
SiO_2	57.76	58.77
Al_2O_3	24.39	19.87
Fe_2O_3	6.27	4.86
CaO	4.64	3.71
MgO	0.82	1.75
K_2O	1.14	0.97
Na_2O	0.39	4.24
TiO_2	1.23	0.57
MnO	0.11	0.08
P_2O_5	0.32	0.15
LOI	2.93	5.03

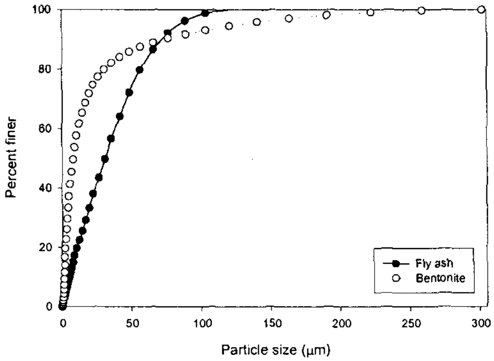

Fig. 1. Particle size distribution of fly ash and bentonite.

Kinetic experiments

Tests were conducted on the kinetics of the adsorption of the lead and cadmium ions onto the two samples. Fig. 2 shows the removal of the two ions from the aqueous solution as a function of time at pH 6. It is obvious that there is a relatively rapid initial rate for adsorption. This rate decreases markedly within 0.5 to 1 hour to give a gradual approach to an equilibrium condition, which is attained after 4 to 8 hours. It can be seen that the rates of adsorption are higher for Sample 2 (mixture of fly ash and bentonite). Cumulative removal of lead is nearly 100 percent, whereas cadmium removal is less than 20 percent for both samples.

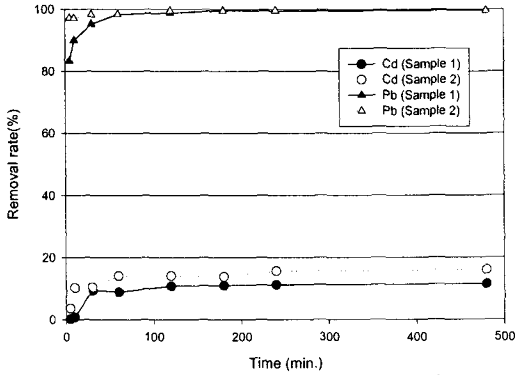

Fig. 2. Temporal change of heavy metal adsorption at pH 6.

Adsorption experiments

The Langmuir isotherm and the Freundlich isotherms were employed to describe the adsorption data for the lead and cadmium ion. The Langmuir isotherm is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \tag{2}$$

where C_e (mg/L) is the equilibrium concentration of metal ions in the solution, q_e (mg/g) is the amount of adsorbed metal ions per unit weight of solid, b (L/mg) is an adsorption constant related to the binding energy, and Q^0 (mg/g) is the maximum amount of metal ions that can be adsorbed by the solid (Gupta et al.,1990).

The Freundlich equation is expressed as:

$$q_e = K_F C_e^n \tag{3}$$

where, K_F (L/g) and n are constants characteristic of the system.

Fig.3 shows the results of analysis by two isotherms. The adsorption data of lead are better fitted by the Langmuir, as shown in Fig. 3(a), whereas the Freundlich isotherm fits the data better for adsorption of cadmium, as shown in Fig 3(b). The corresponding Langmuir and Freundlich parameters along with correlation coefficient are given in Table 3. For lead, the value of b is higher for Sample 1, whereas the value of Q^0 is higher for Sample 2. It indicates that Sample 1 adsorbs the lead ions more quickly than Sample 2, but Sample 2 is capable of adsorbing more ions than Sample 1. For cadmium, the K_F and n values of both samples were similar.

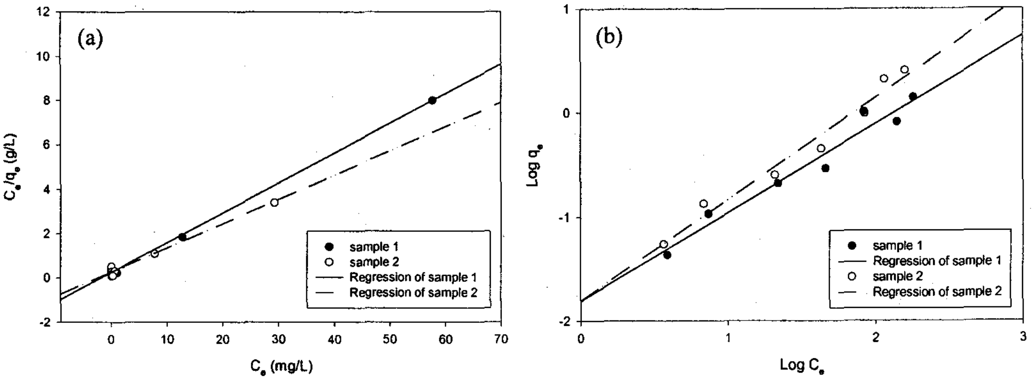

Fig. 3. (a) The Langmuir isotherm for lead; (b) The Freundlich isotherm for cadmium

Table 2. Langmuir and Freundlich isotherm constants of lead and cadmium on Sample 1 and Sample 2.

	Langmuir constants for lead			Freundlich constants for cadmium		
	b (L/mg)	Q^0 (mg/g)	R^2	K_F (L/g)	N	R^2
Sample 1	0.622	7.446	0.9975	0.1636	1.1743	0.9561
Sample 2	0.460	9.285	0.9859	0.1642	1.0246	0.9719

Column experiments

Tracer experiments were performed to determine the hydrogeological parameter values, the seepage velocity (v_x) and the dispersivity (α_L), using lithium bromide. The technique used in this study was based on the so-called method of moments (Fetter, 1999). The concentration of the tracer in the effluent, C, was measured for various pore volumes, U, and then C/C_0 was plotted as a function of $[(U-1)/U^{1/2}]$ on a linear probability paper. The slope of the line is related to the longitudinal hydrodynamic dispersion. The value of the dispersion coefficient (D_L) can be found from

$$D_L = \left(\frac{v_x L}{8}\right)(J_{0.84} - J_{0.16})^2 \tag{4}$$

where

$$J_{0.84} = [(U-1)/U^{1/2}] \text{ when } C/C_0 \text{ is } 0.84$$

$$J_{0.16} = [(U-1)/U^{1/2}] \text{ when } C/C_0 \text{ is } 0.16$$

Since $D_L = \alpha_L v_x + D^*$,

$$\alpha_L = \frac{D_L - D^*}{v_x} \tag{5}$$

The results are shown in Table 3. The seepage velocity obtained from the breakthrough curves is 2.315×10^{-5} m/s for Sample 1 and 1.329×10^{-6} m/s for Sample 2. The dispersion coefficient and the dispersivity of Sample 1 are one or two orders of magnitude higher than those of Sample 2.

The relative concentrations of cadmium and lead in the leachate are presented in Fig. 4(a) and Fig. 4(b) as a function of time. For Sample 2, cadmium did not break though within 90 hours, whereas for Sample 1, cadmium broke thtough within 4 hours. However, when the relative concentrations were plotted against pore volume, the breakthrough curves of the two samples were similar and the breakthrough volume was the same at 10 pore volumes for both samples. The breakthrough time of lead was substantially higher than that of cadmium. For Sample 1, lead did not breakthrough within 125 hours, whereas no breakthrough occurred within 815 hours for Sample 2. Obviously, fly ash was very effective in the retardation of lead, as shown in the adsorption tests. The breakthrough curves of Sample 1 and Sample 2 for lead were again very similar when plotted against the pore volume. Therefore, it can be said that Sample 2 is a better hydraulic barrier, but as a chemical barrier, Sample 1 is as effective as Sample 2.

Table 3. Hydraulic parameters for Sample 1 and Sample 2.

	v_x (m/s)	D_L (m^2/s)	α_L (m)
Sample 1	2.315×10^{-5}	7.871×10^{-8}	3.4×10^{-3}
Sample 2	1.329×10^{-6}	3.323×10^{-10}	2.5×10^{-4}

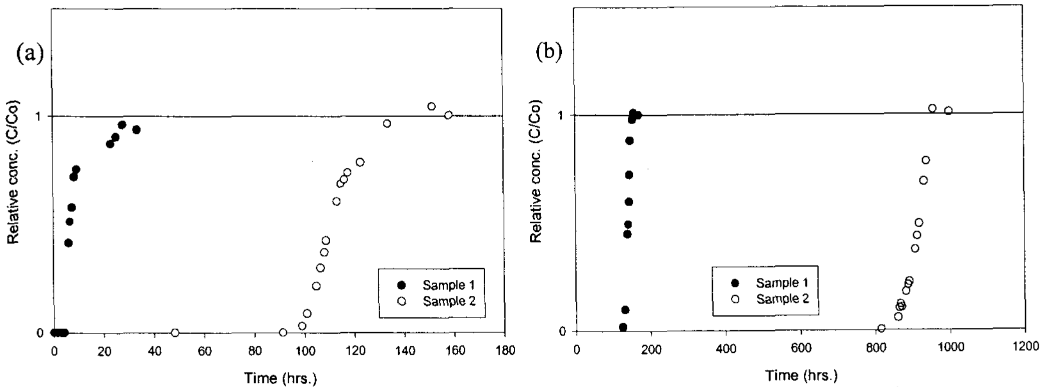

Fig. 4. Breakthrough curves for Sample 1 and Sample 2; (a) Cadmium; (b) Lead

Reactive transport modeling

To simulate the breakthrough curves, the column was divided into 10 elements and all transport simulations were conducted on each element. The initial composition of the pore water in each element and the composition of the input fluid were defined at the same conditions in the column experiments. The adsorptive reactions of cadmium and lead were established using the isotherm parameters in Table 2. In some experiments, adsorption was not sufficiently fast compared to the breakthrough time. Therefore, a nonequilibrium or kinetic sorption process was adopted. When the local equilibrium is not attained, the adsorption process is often represented as a first-order reversible reaction. The adsorption rate of aqueous species c_i is given by:

$$R_i = -k_m(c_i - \frac{s_i}{K_d}) \tag{5}$$

where c_i (mol/L) denotes the aqueous concentration of species, s_i is the sorbed concentration (mol/g), k_m is the mass transfer coefficient (hr^{-1}), and K_d is the distribution coefficient (L/g). The values of the coefficients are given in Table 4. The distribution coefficients are similar to the parameters of the linear isotherm that was fitted for the batch adsorption experiments. In this case, the plot was described using the unit of a mole concentration. The mass transfer coefficient of Sample 2 for cadmium is 0.027 hr^{-1}, which is larger than that of Sample 1. It supports the results shown in Fig. 2. Other possible reactions such as precipitation were included in the simulations, using the thermodynamic paramteers stored in the PHREEQC data base.

Table 4. Kinetic parameters of cadmium on sample1 and sample2.

	Kinetic parameter for cadmium	
	k_m (hr^{-1})	K_d (L/g)
Sample1	0.018	0.0067
Sample2	0.027	0.01

Fig. 5 shows experimental data and the simulated breakthrough curves. It can be seen that the simulated curves are stiffer in shape compared to the experimental data, which indicates that the attenuation of cadmium migration is overpredicted. Better fits are obtained with the lower values of the mass transfer coefficients for each sample. For Sample 1, the value of k_m was reduced to 0.0036 and for Sample 2 it was reduced to 0.0018, which is about 15 times smaller than the values of the batch test results. Rate of adsorption is controlled by several characteristics of the adsorbent, adsorbate, and solution phase. These include particle size of the adsorbent, concentration of the adsorbate, degree of mixing, and diffusion coefficients. Obviously, the physical configuration of the adsorbate and adsorbent systems is quite different between the continuous fixed-bed reactor and the batch stirred tank reactor. This may be a reason why the rates obtained by the batch tests did not give a good prediction for the breakthrough behavior of the column. However, it is possible that the hydraulic parameters including the seepage velocity and dispersity were not correctly estimated, since these parameters are difficult to measure and can vary from sample to sample depending on how well the column is packed with powder.

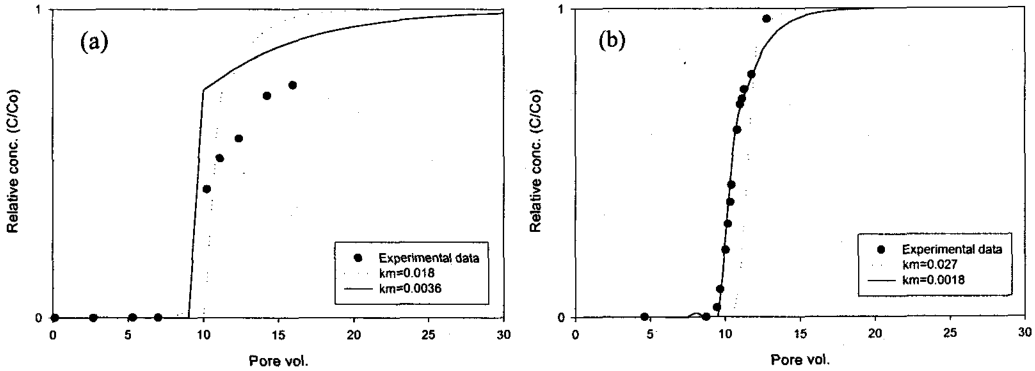

Fig. 5. Breakthrough curves of cadmium with different mass transfer coefficients, k_m, (a) Sample 1; (b) Sample 2

Based on the fitted simulation results, the transport profiles on the various conditions were simulated. The results are presented in Fig. 6. When the initial concentration of input fluid decreased from 50 mg/L to 5 mg/L, the breakthrough time increased by two pore volumes, although the shape of the breakthrough curve stayed almost the same. It suggests that the barrier has a certain saturation capacity of retaining metal ions. As the influent concentration decreases, it takes a longer time to reach the saturation limit, and hence, the breakthrough time is delayed. When the initial pH of input fluid increased from 3.27 to 6, an interesting result was obtained. The breakthrough time was nearly similar to the case when the initial concentration was lowered. But in this case, the breakthrough curve levelled off rather than converge to 1. This suggests that there was some retarding mechanism to hold a portion of the cadmium ion for an extended period of time. It is postulated that the buffering capacity of the sample produced such results. As shown in the chemical composition, the samples are likely to have alkaline solids such as $Ca(OH)_2$ and $CaCO_3$. The alkalinity provided by these materials can increase the pH of the leachate solution to cause precipitation of metals as their respective hydroxides or carbonates. Therefore, the migration of the metal ions through the barrier can exhibit retardation by precipitation based on hydroxide or carbonate formation. However, as the acidic leaching solution progresses through the barrier, the pH of the solution should decrease due to the depletion of the alkaline materials. In turn, the metals held as hydroxides in the barrier material dissolve and eventually break through. However, when the pH of the influent solution is close to neutral, a condition can be established such that buffering capacities given by the alkaline materials maintain a high pH needed for metal precipitation to take place favorably.

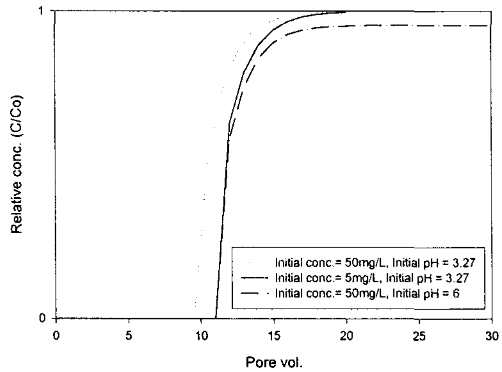

Fig. 6. Comparison of the breakthrough curves on the various conditions.

The long-term performance of the fly ash/bentonite mixture as a landfill barrier was evaluated using the reactive transport model. The model was based on the concept of the advection-dispersion transport coupled with chemical reactions with the barrier. In this simulation, the advective transport was neglected since the barrier under the real condition of the landfill has a very low hydraulic conductivity. Fig. 7 shows the simulation results under the conditions of the influent cadmium concentration of 50 mg/L, the initial pH of 6 and the barrier thickness of 50 cm. It can be seen that the neutralization capacity and the very low level of dispersion transport in the barrier combine, causing significant retardation of mobility of the cadmium ions; the breakthrough appears after 35 years.

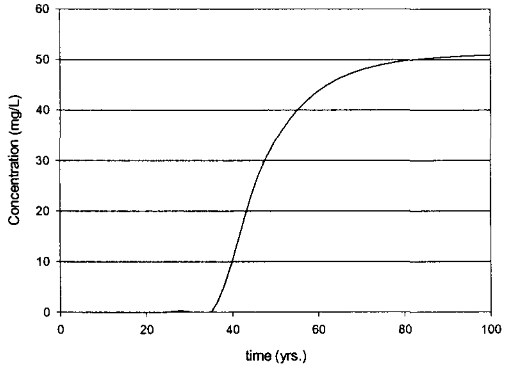

Fig. 7. Simulation under the real conditions of the landfill liner.

4. Conclusions

In this study, the mixtures of fly ash and bentonite were investigated for their ability to attenuate the transport of heavy metal contaminants. Batch adsorption tests showed that cadmium and lead were rapidly adsorbed and the equilibrium was reached in two hours. The fly ash/bentonite mixtures adsorbed almost 100 percent of lead at pH 6. However, cadmium adsorption was low with a saturation adsorption of 20%. The adsorption data of lead fit very well with the Langmuir isotherm whereas the Freundlich model better fit the data for cadmium. The results of the column experiments showed that lead was much better adsorbed than cadmium, in accordance with the results of the batch adsorption tests.

Using the information obtained from the experimental data, a reactive transport modeling was conducted. However, the adsorption parameters obtained from batch tests did not predict the results of the column tests well. Better fits were obtained with lower mass transfer coefficients. Using the corrected parameters, the effects of the concentration and pH of the input fluid were examined. When the cadmium concentration of input solution was reduced ten times from 50 mg/L to 5 mg/L, the breakthrough time increased by 2 pore volumes of leaching. However, the breakthrough profile remained almost the same. This was probably due to the low adsorption rate of cadmium so that the retardation effect did not affect the migration profile to a great extent. Increasing the pH of the input fluid also delayed the breakthrough time. Interestingly though, the breakthrough curve levelled off at a concentration value less than the input. It was postulated that this resulted from the buffering capacity of the sample. Finally, simulation under the realistic conditions of a landfill showed that the mixture of fly ash and bentonite cadmium effectively retarded the migration of cadmium with no breakthrough occurring within 35 years.

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