Migration of calcium hydroxide compounds
in construction waste soil

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Abstract.   Migration of leachate generated through embankment of construction waste soil (CWS) in low-lying areas was studied through physical and chemical analysis. A leachate solution containing soluble cations from CWS was found to have a pH above 9.0. To determine the distribution coefficients in the alkali solution, column and migration tests were conducted in the laboratory. The physical and chemical properties of CWS satisfied environmental soil criteria; however, the pH was high. The effective diffusion coefficients for CWS ions fell within the range of $0.725 - 3.3 \times 10^{-6}$ cm^2/s. Properties of pore water and the amount of undissolved gas in pore water influenced advection–diffusion behavior. Contaminants migrating from CWS exhibited time-dependent concentration profiles and an advective component of transport. Thus, the transport equations for CWS contaminant concentrations satisfied the differential equations in accordance with Fick's 2nd law. Therefore, the migration of the contaminant plume when the landfilling CWS reaches water table can be predicted based on pH using the effective diffusion coefficient determined in a laboratory test.

1. Introduction

   Construction waste landfilling has recently been associated with increasing environmental issues due to larger quantities of waste. Although annual generation of construction waste has decreased in Germany and Japan, it has increased in the United Kingdom, Italy, the Netherlands, Switzerland, and Korea. Construction waste has been increasing in these countries because of the redevelopment of buildings and urban infrastructure (OECD 2015). Most of the aggregate from the demolition of buildings is reused through separation and recycling of usable materials in the construction field. Since most construction waste cannot be landfilled because of environmental concerns, construction waste soil (CWS) is increasingly being used in construction projects as landfilling material. However, although use of recycled concrete aggregate and CWS has increased at construction sites, the quality of these materials has not been verified. It is unclear whether

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recycled aggregate and CWS contain contaminants that are hazardous. Aggregate and CWS are of particular concern because of the amount of small cement particles on the surface. Therefore, landfilled sites using recycled material must be managed to reduce migration of contaminants from recycled aggregate or soil.

Recycled concrete aggregate and CWS contain high concentrations of alkali metals and alkaline earth metals that can change the pH of groundwater and natural soil. Leachate from the recycled aggregate and soil can have a pH above 9.0. Most studies of chemical fate and transport of gas in soil associated with the soil cover zone were conducted for the mining industry, in which wastes and tailings typically produce an acidic leachate when reactive minerals come into contact with water and oxygen (Nicholson *et al.* 1989, Yanful 1993, Aachib *et al.* 2004). The effects of pH on adsorption of inorganic contaminants to metal oxide surfaces have primarily been simulated using surface complexation models (Zheng and Wang 1999, Khan *et al.* 2009, Genc and Ulupinar 2010). Distribution factors for contaminants under these conditions have been previously calculated (Goodall and Quigley 1977, Quigley *et al.* 1987, Shackelford 2014). Diffusion models have been analyzed through many experimental results (Kozaki *et al.* 2005, Liu *et al.* 2003, Van Loon *et al.* 2005, Glaus *et al.* 2007, Bourg *et al.* 2007). This experimental approach is complex compared to the use of simpler analytical models such as the Langmuir and Freundlich isotherms (Hingston 1970, Raven *et al.* 1998, Kundu and Gupta 2006, Thirunavukkarasu *et al.* 2003, Jeppu and Clement 2011). Adsorption of the divalent cations of alkaline earth metals is stronger than that of monovalent alkaline cations; thus, the effective diffusion coefficients for monovalent cations are larger than those for divalent cations. Therefore, monovalent cations predominantly migrate through advection-diffusion behavior in soils with low permeability like silty sand. Some in situ techniques have been proposed to determine diffusion coefficients in the vadose zone of soils (Shackelford and Daniel 1991, Shackelford and Daniel 1991a, Davis *et al.* 2009, Shackelford and Moore 2013). However, it is generally easier and more convenient to evaluate the advection–diffusion coefficient, D_e, using representative samples under well-controlled conditions in the laboratory. Available laboratory techniques have been described by a number of authors (Shackelford and Daniel 1991b, Yanful 1993). The experimental set-up used in this study was based on Shackelford (1991) and Illangasekare *et al.* (2006).

This study focused on the migration of alkaline chemicals in soil in the laboratory. Mass transfer processes were investigated to determine the distribution factor. Hydraulic calcium compounds in cement are a substantial environmental concern where reactive minerals are exposed to groundwater conditions, and were simulated in this study. Their flux is controlled by the effective advection–diffusion coefficient D_e; as the value of D_e decreases, oxygen flux also decreases. The transport of contaminants from a soil cover is therefore strongly related to D_e. To analyze migration of contaminants from CWS, physical properties, chemical compounds, and environmental influences were investigated. The pH of construction waste increased through pozzolanic reactions between calcium oxide and hydroxide ions and was strongly affected by calcium carbonate and alkaline earth cations. The effective distribution was determined by incorporating heterogeneity through fracturing. Transient and pseudo-steady-state matrix-fracture interactions were characterized by predicting trends in the distribution factor over time. The results of this study can be applied to modify the equivalent mass transfer distribution factor to include variable CWS distribution effects and for calibration of porosity models.

2. Theory

2.1 Chemical reactions and pH in construction waste soils

The chemical process that determines the properties of hydraulic cement is hydration. Hydraulic cement, such as Portland cement, is composed of a mixture of silicates and oxides, including belite ($2CaO \cdot SiO_2$), alite ($3CaO \cdot SiO_2$), celite ($3CaO \cdot Al_2O_3$), and brownmillerite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$). Through hydration with water, tobermorite gel ($3CaO \cdot SiO_2 \cdot 3H_2O$) and calcium hydroxide ($Ca(OH)_2$) are formed. Finally, tobermorite forms calcium silicate hydrate (H_2CaO_4Si) and calcium sulfoaluminate through a reaction with celite. The silicates are responsible for the mechanical properties of the cement, while the celite and the brownmillerite are essential in allowing formation of the liquid phase during cooling. In contrast, when non-hydraulic cement, such as calcium hydroxide, is mixed with water, it hardens through carbonation. The calcium oxide (CaO) in cement generates 15.6 kcal/mol of heat through reaction with pore water in the soil to form calcium hydroxide ($Ca(OH)_2$). The chemical reaction is as follows

$$CaO + H_2O \rightarrow Ca(OH)_2 + 15.6\,kcal/mol \tag{1}$$
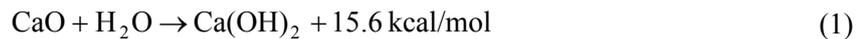
When CWS is soaked in water, the cement paste attached to the aggregate becomes a calcium hydroxide solution. $Ca(OH)_2$ produces calcium carbonate ($CaCO_3$) through a reaction with CO_2. At high concentrations of CO_2, $CaCO_3$ reacts with CO_2 to form calcium bicarbonate ($Ca(HCO_3)_2$). Iteration of this reaction gradually neutralizes the pH. The reaction steps are as follows

$$2(CaO)_2 + SiO_2 + 6H_2O \rightarrow (CaO)_3(SiO)_2(H_2O)_3 + 3Ca(OH)_2$$
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{2}$$
$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$
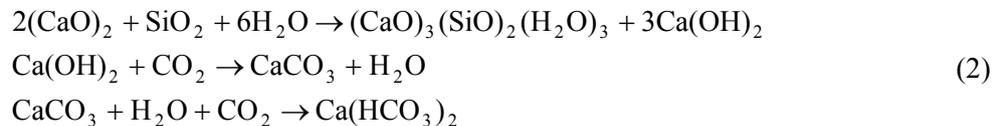
The $CaCO_3$ dissociates to calcium and carbonate ion (CO_3^{2-}). The carbonate ion reacts with water to form bicarbonate ion (HCO_3^-) and hydroxide ion (OH^-). CO_3^{2-} and HCO_3^- are basic ions that generate hydroxide ions in these reactions increase the pH as shown below

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$$
$$CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^-$$
$$HCO_3^- + H_2O \leftrightarrow H_2CO_3 + OH^- \tag{3}$$
$$H_2CO_3 \leftrightarrow H_2O + CO_2$$
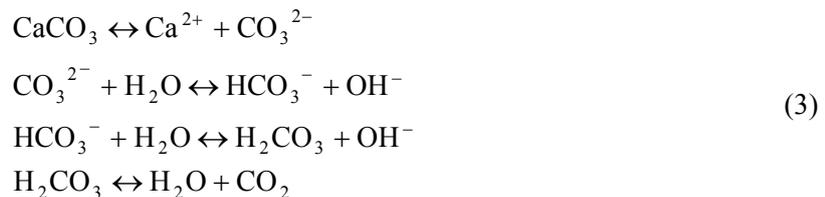
The hydroxide produced from the calcium carbonate reactions in water induces an increase in pH, while the alkali metal and alkaline earth metal chemical ions in the solution buffer the pH concentration to maintain a basic solution.

2.2 Contaminant transport by advection and diffusion

Contaminant transport through porous media mainly occurs through molecular diffusion and advection. In the fine-grained soils used as landfill cover, contaminants tend to migrate mainly by

molecular diffusion (Yanful 1993). For a hydroxide ion (OH⁻), this diffusion occurs in the aqueous phase of the soil. In contrast, advection is the process by which solutes are transported along with flowing fluid, typically water, in response to a gradient in the total hydraulic head.

In advection, the fluid transports a conserved quantity or material via bulk movement. The transported material is described by a scalar field showing its distribution over space and does not include transport of substances by molecular diffusion. The advection mass flux can be expressed as follows

$$J_A = v \cdot c = \frac{k}{n} ic \tag{4}$$

Where J_A = the advective mass flux (mol/m²s), c = the concentration of the solute in the liquid phase (mol/m³), k = the hydraulic conductivity (m/s), i = the hydraulic gradient, and n = porosity.

For the one-dimensional diffusion process applicable to landfill cover, the hydroxide flux is defined by Fick's first law. When CWS is in contact with ground water, some chemicals in the CWS dissolve into the water. Diffusion may be thought of as a transport process in which a chemical or chemical species migrates in response to a gradient in its concentration. Diffusion in solution typically is assumed to occur in accordance with Fick's first law, which for one-dimensional flow over time can be expressed as follows (Quigley *et al*. 1987)

$$J_D = -D_0 \frac{\partial c}{\partial x} \tag{5}$$

$$\frac{\partial c}{\partial t} = D_s \left(\frac{\partial^2 c}{\partial x^2} \right) \tag{6}$$

Where, J_D = the diffusive mass flux (mol/m²s), x = the distance in the direction of transport (m), D_0 = the diffusion factor in free solution (m²/s), and D_s = the effective diffusion factor which includes the chemical and biological retardation factors in the soil pore water ($D_0 \cdot \tau / R_d$). The effective diffusion coefficient, D_s, for solutes diffusing in soil can be calculated based on the free solution diffusion factor, D_0, and the tortuosity factor τ (Shackelford 1991). The diffusion factors, D_s, used to back calculate these values were taken from reference in free solution and are presented in Table 1 along with approximate distribution factor values, K_d, assuming that Cl⁻ is a conservative species for determining τ. For reference, $\tau_{\_cl}$ has been estimated to be 0.32 at 25°C and 50.51 at 7°C (Yanful 1993).

Table 1 Diffusion factors in free solution

Cation	Diffusion factor ($\times 10^{-6}$ cm²/s)	Anion	Diffusion factor ($\times 10^{-6}$ cm²/s)
H^+	93.1	OH^-	52.7
Ca^{2+}	7.93	HCO_3^-	11.8
Mg^{2+}	7.05	Cl^-	20.3
Na^+	13.3		
K^+	19.6		

The concentration of a reactive solute subject to reversible sorption reactions during diffusive transport in soil can expressed by Fick's second law including the retardation factor R_d, which is the ratio of the rate of fluid flow to the transport rate of the reactive solute

$$\frac{\partial c}{\partial t} = \frac{D^*}{R_d}\left(\frac{\partial^2 c}{\partial x^2}\right)$$
(7)

Where, D^* = the effective diffusion factor without chemical and biological retardation factor in the soil pore water, R_d = the retardation factor $(1 + \gamma_d \cdot K_p/\theta)$, γ_d = the dry density (mol/m^3), θ = the volumetric water content (m^3/m^3), K_p = the partitioning coefficient (dq/dc), and q = the absorption concentration (mol/m^3). K_p represents the distribution factor, which is the equilibrium concentration in the pore water of the soil.

A plot of q versus c is called an adsorption isotherm. When the relationship between q and c is linear, K_p is termed the distribution coefficient, K_d (Shackelford 1991). The equilibrium concentration in an adsorption isotherm can be determined from a batch equilibrium test in a laboratory.

2.3 Governing equation for advection–diffusion behavior

Advection and diffusion in porous media such as soils, industrials wastes, and mine tailings are the primary processes that determine the migration of chemical species within landfills, particularly when a soil layer is put in place to control fluid exchanges with the groundwater. Derivation of the applicable advection–diffusion equation relies on the principle of superposition. Advection and diffusion can be added together if they are linearly independent. From the second-order differential equation, the mixed Euler–Lagrange equation is as follows

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x_i}\left(D^* \frac{\partial c}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i c) + \sum_{n=1}^{N} R_n$$
(8)

Where, R is retardation due to processes such as adsorption, biodegradation, and radioisotope reactions. From Eq. (7), the retardation factor R can be expressed by the chain rule

$$R = -\frac{\gamma_d}{\theta}\frac{\partial q}{\partial t} = -\frac{\gamma_d}{\theta}\frac{\partial c}{\partial t}\frac{\partial q}{\partial c}$$
(9)

Therefore, Eq. (8) can be represented as

$$\left(1 + \frac{\gamma_d}{\theta}\frac{\partial q}{\partial c}\right)\left(\frac{\partial c}{\partial t}\right) = \frac{\partial}{\partial x_i}\left(D^* \frac{\partial c}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i c)$$
(10)

From Eq. (10), the retardation factor in saturated porous media may be defined as

$$\left(1 + \frac{\gamma_d}{\theta}\frac{\partial q}{\partial c}\right) = R_d$$
(11)

Finally, the governing advection–diffusion equation can be expressed as follows

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x_i}\left(\frac{D^*}{R_d}\frac{\partial c}{\partial x_j}\right) - \frac{\partial}{\partial x_i}vc \tag{12}$$

3. Experimental

3.1 Physical properties of construction waste soils

The soil specimens were collected by NX boring (76-mm diameter) at 56 stations as part of a site investigation of a reclamation site and at 3 additional stations at the aggregate separation company where the CWS was stored in Seo-gu District, Incheon, Korea. Physical and mechanical tests such as water content, grain size, percentage of fines (smaller than No. 200 sieve), specific gravity, liquid limit, plastic limit, plasticity index, compaction test, and bearing test (modified California Bearing Ratio) were conducted in a laboratory test. The particle size was determined using Nos. 4, 8, and 40 sieves. The percent organic matter was also tested to evaluate compliance with the specification that requires organic content to be < 1%.

To evaluate differences in pH with particle size, 250 g of the sample was mixed with 500 mL of water after taking 50 g of the sample from each of 5 replicates, and the pH was measured over time.

3.2 Chemical properties and environmental contaminants of construction waste soil

Portland cement contains chemical compounds such as silica (SiO_2) and alumina (Al_2O_3) from clay, and calcium oxide (quick lime, CaO) from limestone. In saturated cement, $3CaO \cdot SiO_2$ forms tobermorite gel ($3CaO \cdot SiO_2 \cdot 3H_2O$) and $Ca(OH)_2$ through hydration. The chemical compounds $3CaO \cdot Al_2O_3$ and $CaSO_4 \cdot 2H_2O$ produce calcium sulfoaluminate when saturated. Other chemicals formed from tobermorite gel include calcium silicate hydrate and ettringite as calcium aluminate hydrate. The CWS may be mixed with weathered granite soil (WGS) and cement paste aggregates. An image of the surface of the CWS was obtained by scanning electron microscope (SEM) with using a Philips XL-30 ESEM and the major chemical components of CWS and WGS were determined by X-ray fluorescence (XRF) with using a Shimadzu XRF-1500. The detection equipment used in this analysis are OPTIMA 4300DV, Perkin-Elmer (detection limit 10 ppb).

In Korea, CWS used for landfilling is required to satisfy certain environmental criteria. The environmental criteria correspond to limiting chemical concentrations that can impact human health, the environment, agriculture, and livestock. The recycled concrete aggregate was soaked in water for 6 months to analyze the chemical components of the leachate for comparison to the criteria. The instruments used for these analyses were a Perkin-Elmer Optima 4300 DV inductively coupled plasma optical emission spectrometer (ICP-OES; detection limit, 10 ppb) and a Dionex ICS 2000 ion chromatography (IC) system.

3.3 Adsorption isotherms and determination of the effective diffusion coefficient

Soil properties were determined for a saturated soil classified as silty sand (SM) and compared to literature values for clay (CL). In this test, the alkali solution and soil were mixed

homogeneously by stirring at a volume ratio of 10:1. The volumetric water content was calculated using the total porosity after the mean water content for the soil was determined. Adsorption isotherms may be linear, concave nonlinear, or convex nonlinear. The adsorption behavior of the solute concentrations was assumed to be linear. The most widely used analytical isotherms for modeling adsorption in a batch test are the Langmuir isotherm and the Freundlich isotherm (Kundu and Gupta 2006). The Langmuir–Freundlich isotherm, also known as Sip's equation, is a versatile isotherm expression that can simulate both Langmuir and Freundlich behaviors (Nahm *et al*. 1977, Limousin *et al*. 2007). After equilibration, water samples from each batch were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and tracer isotherms were developed.

The experimental procedure for alkali ions described by Quigley *et al*. (1987), Shackelford (1991), and Yanful (1993) was used to determine the effective diffusion coefficient D^* based on a decreasing source concentration with time.

4. Results and discussion

4.1 Physical and chemical properties

The results of the physical tests are presented in Table 2. Passing rate of 0.8 mm exceeds only the criterion in NH-3 specimen in which consistency is non-plastic. Unit weight and CBR, which were determined in a laboratory test, satisfied the criterion for landfilling.

The particle distribution curves for the CWS are shown in Fig. 1. The particle size distribution curves represent well graded soil in which particle size was distributed over a wide range and partially fine sand have a combination in CWS (1) and CWS (3).

Fig. 2 shows an image of the surface of the CWS obtained by SEM at 1000×. The major chemical components of CWS and WGS as determined by XRF are listed in Table 3. WGS was determined to be primarily silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3). In the CWS, most of the surface particles were calcium silicate hydrate.

Table 2 Physical and mechanical properties of construction waste soil

Property		NH-1	NH-2	NH-3	Criterion
Passing rate (%)	4.75 mm	82.5	75.7	82.5	25–100%
	0.08 mm	20.0	19.8	29.9	0–25%
Liquid limit (%)		NP*	NP	NP	< 50%
Plastic limit (%)		NP	NP	NP	< 25%
Plasticity index		NP	NP	NP	-
Water content, ω (%)		12.1	11.4	20.7	-
Void ratio, e (%)		31.4	31.5	31.9	< 42
r_{dmax} (kPa/m^3)		18.39	18.30	18.19	> 1.5
Modified CBR (%)		19.3	18.8	17.4	2.5
Organic material content (%)		0.17	0.14	0.16	< 1%

*NP: Non-plastic
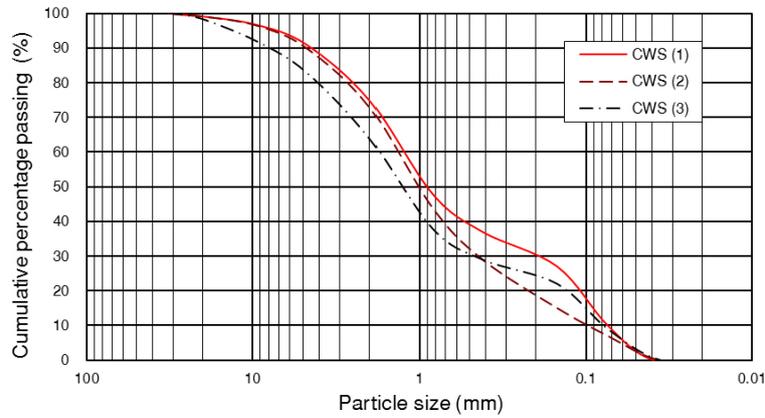
Fig. 1 Typical particle size distribution of construction waste soil
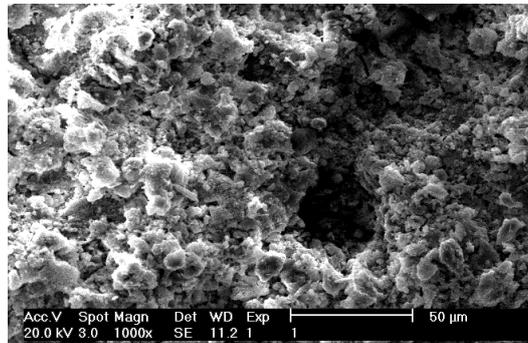
Fig. 2 Scanning electron microscope image of construction waste soil

Table 3 Chemical components of construction waste soils and weathered granite soils

Soil	O	Si	Ca	Al	Fe	K
CWS	45.14	25.36	12.96	8.81	6.13	3.45
WGS	42.46	30.37	0.73	11.92	9.13	3.50

Table 4 Chemical components of construction waste soil solutions

Chemical component	Concentration (mg/L)	
	1	2
Ca	35.36	83.37
Al	3.98	0.80
K	166.7	39.55
S	11.67	29.83
Si	17.48	7.77
Na	85.43	42.98
Cl	15.17	66.4
N	2.35	11.8

The results of chemical analysis of CWS using ICP-AES and IC are shown in Table 4. Alkali metal and alkaline earth metal ions such as potassium, sodium, and calcium were detected at high concentrations.

Concentrations of 21 environmental contaminants found in CWS that could be harmful to human health are presented in Table 5. Among the heavy metals, low concentrations of cadmium, arsenic, mercury, lead, and nickel were detected, but hexavalent chromium was not. Copper, zinc, fluorine, and total petroleum hydrocarbons were detected at higher concentrations than the other analyzes. Phenols, polychlorinated biphenyls, benzo(a)pyrene, organophosphorus compounds, and cyanogens also were not detected. Low concentrations of organic compounds such as benzene, toluene, ethylbenzene, xylene, and trichloroethylene were found. Overall, the soil containing CWS does not require an environmental impact assessment because it meets the Korean environmental criteria.

4.2 Differences in pH with particle size and cation exchange capacity

The pH clearly varied with particle size. Particle size > 4.75 mm without fine-grained silt or clay generated the maximum pH of 9.5 (Fig. 3). Based on the pH tests using CWS with alkaline

Table 5 Environmental contaminant concentrations in construction waste soils

Contaminant	Concentration (mg/kg)			
	Category	NH-1	NH-2	NH-3
Cd	60	0.8	1.3	0.8
Cu	2000	30.3	37.2	33.5
As	200	3.7	6.6	2.4
Hg	20	0.07	0.12	0.09
Pb	700	41.0	71.8	51.3
Zn	2000	187	266	212
Cr^{6+}	40	-	-	-
Ni	500	13.3	12.9	15.3
F	800	112	161	160
P	30	-	-	-
Polychlorinated biphenyls	12	-	-	-
Cyanogen	120	-	-	-
Phenol	20	-	-	-
Benzene	3	0.1	-	-
Toluene	60	0.5	0.3	0.4
Ethylbenzene	340	0.1	-	0.1
Xylene	45	0.3	0.2	0.2
Total petroleum hydrocarbons	2000	53	23	37
Trichloroethylene	40	0.6	0.2	0.7
Tetrachloroethylene	25	0.1	0.1	0.1
Benzo(a)pyrene	7	-	-	-
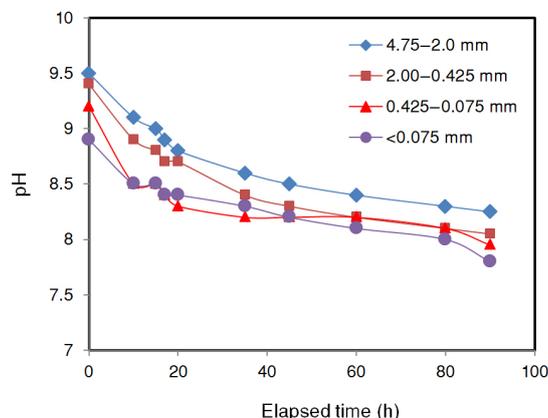
Fig. 3 Correlation in the pH of construction waste soil by particle size

earth chemicals, both particle size and colloid content < 1 μm have a significant effect on pH. The relationship between pH and particle size is somewhat obscured because the colloids in solution affect the pH. Fine-grained soil contains more colloids that adsorb anions compared to coarse-grained soil. The isotherm was relatively linear for alkali solution < 1%.

Ion exchange is a surface chemical phenomenon that is influenced by a number of variables. In an ideal crystal, the positive and negative charges would be balanced. Clay particles carry a net negative charge. To balance the negative charge, the clay particles attract positively charged ions from salts in pore water. The cation exchange capacity of clay is defined as the amount of exchangeable ions in units of cmol$^+$/kg. Cation exchange is one of the major factors in reducing pH. Therefore, the closed system in this test was allowed to approach equilibrium and the cation exchange coefficients were calculated from the slopes of the isotherm graphs. The cation exchange capacity of clay with colloids was found to be ~10 cmol$^+$/kg. In the hydrometer test using Ca^{2+}, K^+, Mg^{2+}, and Na^+, Ca^{2+} was most strongly adsorbed. Exchangeable Ca^{2+} was determined to be 23.5 cmol$^+$/kg. Exchangeable cations for Mg^{2+}, Na^+, and K^+ were 1.0, 0.36, and 0.53 cmol$^+$/kg, respectively (Table 6). The exchange cation capacity of the clay specimen was 11.5 cmol$^+$/kg and organic content was 10%.

4.3 Adsorption isotherms and determination of the effective diffusion coefficient

The final water content and degree of saturation were higher than the initial values. Shackelford reported diffusion coefficients for each soil type through test series 8 (Shackelford 1991). The test

Table 6 Cation exchange capacity and exchangeable concentrations at equilibrium

Exchangeable cation	Concentration (cmol$^+$/kg)
Exchangeable Ca^{2+}	23.5
Exchangeable Mg^{2+}	1.0
Exchangeable Na^+	0.36
Exchangeable K^+	0.53

Table 7 Comparison of soil properties in the effective diffusion test

Property	Soil condition	
	Specimen	Shackelford
Water content, ω (%)	28	25–37
Total porosity, n	0.35	0.47
Degree of saturation, S (%)	98	86.2–90.7
Volumetric water content, θ	0.35	0.41
USCS soil type*	SM	CL

*CL, clay; SM, silty sand; USCS, Unified Soil Classification System
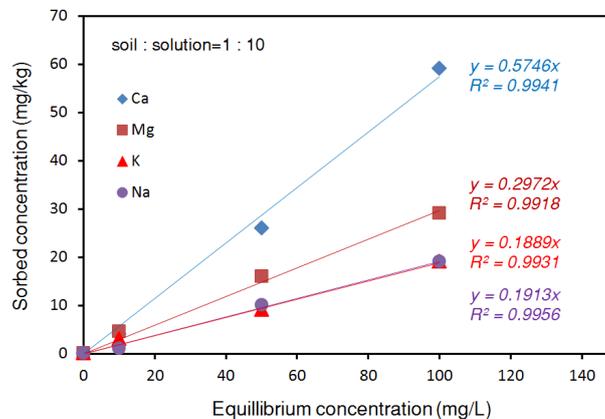
Fig. 4 Changes in the sorbed concentration of alkali ions with equilibrium concentration

results for soil properties are compared to the Shackelford experimental data in Table 7.

Initially, cation adsorption was expected to occur as a linear isotherm in soil, particularly for CWS, which has a pH-dependent adsorption capacity. Calcium ions migrated by advection from the source to the collection reservoir. A tracer isotherm for calcium obtained from the batch tests shows the Langmuir–Freundlich isotherm. Because the adsorption isotherms were linear, the trend lines were used to estimate the retardation factors based on the distribution coefficient K_d. The coefficients K_d obtained through the laboratory tests are shown in Fig. 4, which compares the calculated concentrations of alkali ions with their equilibrium concentrations for the solution in silty sand. After the concentrations reached equilibrium, the advection-diffusion coefficient was calculated from these regressions. The retardation factor R_d was then determined using Eq. (11).

In soils, the diffusion coefficient decreases as the water content increases and reaches a minimum under fully saturated conditions. The effective diffusion coefficient was confirmed through advection–diffusion behavior based on the soil type and adsorption characteristics of the migrating particles. The advection-diffusion behavior showed linear characteristics at low concentrations. D^* was also strongly influenced by the degree of saturation and porosity. The effective diffusion coefficients D^* shown in Table 8 were calculated from the distribution coefficients K_d using the laboratory test results. Distribution is inversely proportional to diffusion and the diffusion coefficient of monovalent ions is larger than that of divalent ions. In the test, potassium had the highest effective diffusion of the cations in alkali solution.

Table 8 Effective diffusion and distribution coefficients based on the diffusion test

Ion	Coefficient	
	D^* ($\times 10^{-6}$ cm^2/s)	K_d (cm^3/g)
Cl$^-$	6.496	0
Ca^{2+}	0.725	0.567
K$^+$	3.30	0.183
Mg^{2+}	0.916	0.298
Na$^+$	2.223	0.186

Table 9 Comparison of effective diffusion coefficients

Ion	D^* ($\times 10^{-6}$ cm^2/s)		
	C1*	C2	C3
Cl$^-$	6.496	4.7	6.47
Ca^{2+}	0.725	-	5.71
K$^+$	3.30	19.6	0.35
Mg^{2+}	0.916	-	3.65
Na$^+$	2.223	-	2.28

*C1: Laboratory test result; C2: Shackelford *et al*. (1991b); C3: Quigley *et al*. (1987)

4.4 Comparison of diffusion coefficients

A summary of the chemical properties for various species is presented in Table 9, comparing the results of this study with those reported in the literature. The range of effective diffusion coefficients was smaller for highly adsorbed ions, but increased for less adsorbed ions. The diffusion coefficients were calculated at 50% of the initial concentration. Quigley *et al*. (1987) and Shackelford (1991) reported effective distribution coefficients for various species, including Cl$^-$, Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+}. In the results for C1, the data points did not precisely fit the regression because the initial concentration was decreasing with time. The present effective diffusion coefficients were similar to those in the literature, but the coefficient for K$^+$ in C2 was higher than the others.

In the present laboratory tests with clayey silt, the effective diffusion coefficient for Cl$^-$ had the highest value of 6.496, similar to the test value for C3. The coefficient for K$^+$ was the highest among the alkali ions. Na$^+$ had a value similar to that of C3; however, the effective diffusion coefficients for Ca^{2+} and Mg^{2+} were lower than those reported previously using the monovalent ion test.

5. Conclusions

CWS in low-lying areas was tested to determine a variety of advection and diffusion parameters. The components of CWS and concentrations of environmental contaminants were determined by physical and chemical analyses. Changes in the pH of ground water were measured

during advection and diffusion of ions in alkaline solution. Conclusions regarding migration of CWS constituents after landfilling are as follows:

(1) In the laboratory tests with CWS, the particle distributions of the recycled soil showed 19.8–30% passing the 0.075-mm sieve. However, such fine-grained soils may exceed engineering specifications. Therefore, the CWS may need to be mixed with coarser-grained soil for use as landfill material in construction projects.

(2) The measured effective diffusion coefficients ranged from 0.725 to 3.3×10^{-6} cm^2/s. Due to the time-dependence of the concentration profiles, the CWS transport equations for the cation concentrations satisfied the differential equations of Fick's 2nd law. Therefore, contaminant plumes from CWS used as landfill material can be predicted based on the pH using the effective diffusion coefficients derived from the results of the laboratory tests.

(3) The pH of CWS may exceed 9.0 and remains continuously high due to the chemical reactions of the cement paste constituents. Therefore, pH is an important factor to consider in protecting against environmental degradation.

Acknowledgments

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