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Doctoral Dissertation

Evaluating the Mechanical and Diffusive Leaching
Performance of Cement-Stabilized Clay Mixed with
Recycled Concrete Aggregates

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Abstract

In Japan, ground stabilization techniques often used cement as a stabilizer, due to its local availability and ability to achieve sufficient compressive strength in a short time. To reduce costs and CO₂ emissions from cement use while promoting waste recycling, recycled concrete aggregate (RCA) from construction and demolition waste has been adopted as a supplementary material. However, the use of waste-derived materials and cement raises environmental concerns due to the presence of hexavalent chromium (Cr(VI)) and other chemicals. Thus, their leaching should be appropriately evaluated and controlled. The objectives of this research addresses three related technical issues; 1) to investigate the leaching of Cr(VI) from compacted cement-stabilized clay (SC) and the influential factors, 2) to assess both mechanical and leaching performances of stabilized clay compacted with RCA; and 3) to conduct analytical modeling of environmental impact by leaching from the compacted stabilized clay with RCA.

In chapter 1, the objectives and scope of this work were clarified.

In chapter 2, the mechanical performance, internal structure, and transport of heavy metal contaminants within RCA-clay mixtures were reviewed. The significance of diffusion in the migration of heavy metal contaminants was emphasized, with particular focus on key parameters such as the effective diffusion coefficient (D_{eff}), partitioning coefficient (K_d), and their experimental determination.

In chapter 3, The investigation of Cr(VI) concentration from stabilized soil with cement was conducted by tank leaching tests (TLTs) for immersing specimen for 28 days. In addition, the influencing factors on leaching of Cr(VI) such as mixing methods, curing periods, specific surface areas of the specimens, and liquid-to-solid ratios were investigated. Specimens of wet mixing method (WM) exhibited significantly lower Cr(VI) leaching than specimens of dry mixing method (DM) with the equivalent unconfined compression strength, due to improved

homogeneity and cement hydration. Specimens cured for 28 days showed lower Cr(VI) leaching compared to those cured for 7 days due to enhanced Cr(VI) precipitation from hydration products over time. Leaching rates were also affected by the specific surface area, suggesting a need to revise Japanese TLT regulations for the cement-stabilized soil to better account for these factors.

In chapter 4, after mixing the RCA to SC with varying RCA contents (20%, 40%, and 60% by weight), laboratory experiments, including Proctor compaction tests, hydraulic conductivity tests, batch leaching tests (BLTs), and TLTs with periodic replacement of the leach solution, were conducted. These tests revealed that RCA improves the compaction performance of SC-RCA mixtures and reduces hydraulic conductivity (K). The minimum void ratio was achieved at 60% RCA, while the lowest K was observed at 40% RCA since the effective compaction of soil fraction was achieved. Higher RCA content led to increased Cr(VI) leaching in BLTs, but negligible leaching in TLTs. Calcium (Ca) was measured in TLTs to further determine D_{eff} . D_{eff} values decreased as RCA content increased; however, for specimens with 60% RCA, D_{eff} increased due to better pore connectivity, which facilitated faster diffusion of Ca.

In chapter 5, the experimental parameters of compacted SC-RCA mixtures were adopted to predict the long-term leaching behavior of Ca and Cr(VI) through FE analysis. The results revealed that that Ca and Cr(VI) concentrations at the point of concern was effectively limited by mixing compacted SC with 40%-RCA due to its lowest D_{eff} . However, the increasing RCA content in compacted SC-RCA mixtures extended the leaching period for Ca due to higher adsorption (K_d values), while Cr(VI) leaching remained consistent across mixtures as K_d values showed minimal variation.

In chapter 6, the main conclusions and recommendations for future work were summarized

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Chapter 1: Introduction

1.1 Background

Soft clay presents significant geotechnical challenges in construction due to its undesirable properties, such as high compressibility, low shear strength, and high-water content. In Japan, techniques for improving the mechanical properties of clay are widely researched to meet construction objectives. Ground stabilization techniques used cement as a stabilizer, commonly applied in road construction and extensively studied. Cement-stabilized sludge is a common stabilizer, locally available and capable of achieving sufficient compressive strength in a short period. However, the construction cost and environmental impact associated with cement manufacturing are prompting scientists and national governments worldwide to explore alternative construction materials. In recent decades, the global rise in construction material production and consumption has led to significant environmental pollution. This issue can be examined from three key perspectives:

- The extraction and production of natural construction materials consume energy, primarily from fossil fuels, generating carbon emissions and other greenhouse gases (Disfani et al., 2014; Akhtar & Sarmah, 2018).
- Natural construction materials are finite, and overexploitation may cause irreversible environmental damage (Agrela et al., 2012).
- Landfilling and accumulation of construction and demolition (C&D) waste lead to contamination and ecological concerns (Agrela et al., 2012; Jiménez et al., 2012).

Currently, Research on sustainable alternative materials for construction is a key trend in Japan and is receiving significant attention and support. One sustainable alternative materials idea is the recycling and reuse of C&D wastes. This approach not only assists in offsetting

environmental pollution but also contributes to preserving the Earth's natural resources. In recent decades, numerous researchers have studied the use of recycled aggregates as pavement construction materials. Their findings suggest that RCA can effectively replace natural aggregates in pavement applications. (Maghool et al., 2017; Arulrajah et al., 2020; Imteaz et al., 2020).

Japan's Construction Material Recycling Law, enacted in 2000, encourages sustainable development by addressing the challenges posed by limited natural resources. The concept of 3Rs (Reduce, Reuse, and Recycle) aim to establish a "material-cycle society" by efficiently utilizing waste and minimizing landfill disposal. Given the construction industry's significant waste generation, efforts to reuse and recycle materials have led to notable progress.

The use of cement-stabilized clay (SC) and C&D waste, such as Recycled Concrete Aggregates (RCA), raises environmental concerns due to the presence of hexavalent chromium (Cr(VI)). Research indicates that cementitious materials contain Cr(VI), partly formed by the oxidation of trivalent chromium Cr(III) in raw materials like clay and limestone at high temperatures in cement kilns (Bae et al., 2017). Therefore, a thorough assessment of factors influencing Cr(VI) release is crucial to understanding its environmental impact.

Considering, the leaching mechanism in compacted SC containing RCAs is mainly controlled by diffusion (Shackelford & Daniel, 1991b). Further analysis involves the calculation of the apparent diffusion coefficient (D^{app}) and effective diffusion coefficient (D_{eff}) of the solute. Generally, D^{app} differs from D_{eff} . D^{app} refers to the overall rate at which chemicals of concern (COCs) in solute appear to diffuse through the soil, while D_{eff} measures the rate at which the COCs in solute diffuse through the pore spaces of the soil, accounting for the tortuosity and connectivity of the pores. D_{eff} can be calculated using D^{app} with a retardation effect, which considers interactions between the solute and the soil matrix that may reduce the actual diffusion rate compared to what would be expected based on D^{app} solely.

This research investigates the leaching of Cr(VI) from compacted cement-stabilized clay (SC) and the addition of recycled concrete aggregate (RCA) to enhance its mechanical performance while limiting diffusive leaching. Although existing studies highlight the potential of RCA to mitigate undesirable properties of clay, such as low shear strength and high compressibility, most previous research has focused on the mechanical aspects of RCA-reinforced clay materials. Recognizing the environmental impact, this study further explores the diffusive leaching behavior of SC and RCA to promote both environmentally sustainable and economically viable secondary material utilization.

1.2 Research Objectives

The main objectives of this research are as follows:

1. To conduct a preliminary investigation of Cr(VI) leaching from compacted cement-stabilized clay and identify the factors influencing this leaching.
2. To assess the mechanical and leaching performance of incorporating RCA into compacted SC.
3. To predict the long-term leaching behavior of Cr(VI) and Ca through analytical modeling and to propose practical applications for compacted SC-RCA mixtures.

1.3 Research Scope

This research initially investigates certain amounts of Cr(VI) leaching from cement-stabilized soil, and additionally examines factors such as dry and wet mixing methods, curing periods, different specimen surface areas, and liquid-to-solid ratios.

Subsequently, recycled concrete aggregate (RCA) will be added to compacted cement-stabilized clay (SC) in varying amounts (20%, 40%, and 60% by weight) to enhance mechanical performance and reduce leaching performance. Experimental studies, including Proctor

compaction tests, hydraulic conductivity tests, batch leaching tests, tank leaching tests, and L/S-parallel leaching tests, have been conducted to support this approach.

Finally, the experimental parameters of compacted SC-RCA mixtures will be used to estimate the long-term leaching behavior of calcium (Ca) and Cr(VI) through analytical modeling using HYDRUS.

1.4 Organization of Thesis

This research consists of six chapters, with summaries for each outlined below:

Chapter 1 serves as an introduction, highlighting the significance of this research while outlining its objectives and scope.

Chapter 2 provides a literature review of recent research papers involving the sustainable reuse of RCA and SC. This includes an exploration of the environmental impact on Cr(VI) leaching from those materials and the factors influencing its leaching, incorporating discussions on solute transport mechanism and significance of Diffusion on Migration of Chemicals. In this chapter, square brackets are used to represent the fundamental dimensions of mass (M), length (L), and time (T) to ensure dimensional consistency in equations.

Chapter 3 investigates the leaching behavior of Cr(VI) from cement-stabilized soil. Additionally, it examines the factors influencing Cr(VI) concentration, such as specific surface area, specimen homogeneity, liquid-to-solid ratios, and curing periods in compacted cement-stabilized soil.

Chapter 4 investigates the improved compaction and hydraulic performances of cement-stabilized clay using recycled concrete aggregates. The study focused on the compaction and hydraulic performances of SC under various RCA contents. Additionally, it investigates the leaching of Cr(VI) and analyzes the diffusive leaching performance of compacted SC-RCA mixtures.

Chapter 5 presents modelling to show the long-term leaching behavior of calcium (Ca) and Cr(VI), as well as practical applications. The parameters obtained from the previous section, along with certain parameters from the literature review, were incorporated into the analytical modeling.

Chapter 6 presents the research conclusion and recommendations for future studies.

Chapter 2: Literature Review

2.1 Cement-Stabilized Clay

Clay stabilization with cementitious additives through in-situ mixing or grouting is a common ground improvement technique. While cement and lime are the primary stabilizers, various other materials can also be used. In Japan, commercially available cement-based stabilizers, primarily composed of ordinary Portland cement with pozzolanic and hydration additives like blast furnace slag, sludge, and gypsum, support the 3Rs concept while enhancing specific properties.

Phan et al. (2022) reported that the potential of paper sludge as a supplementary material for cement in stabilizing dredged clayey soil, primarily due to its high water absorption and retention capacity. When processed into paper sludge ash, it functions as a water-absorbing agent, effectively lowering the moisture content of clay. This reduction in water content decreases the free water-to-cement ratio by weight, ultimately enhancing the strength and stability of the treated clay. These findings suggest that incorporating paper sludge ash in soil stabilization can improve performance while promoting sustainable material utilization.

Yoobanpot et al. (2017) suggested that cement kiln dust (CKD) as a valuable industrial byproduct from cement manufacturing. CKD primarily consists of silica, calcium carbonate, calcium sulfate, and calcium oxide (free lime), with minor amounts of sulfates and chlorides. When mixed with clay, the free lime in CKD reacts with water, initiating hydration and a pozzolanic reaction that forms calcium silicate hydrates (CSH). Additionally, scanning electron microscopy revealed the presence of ettringite, monosulfate, and syngenite, highlighting CKD's potential as a stabilizing agent for clay soils.

The SC is also utilized as a geotechnical material in Japan's land reclamation projects to address the ongoing shortage of available land. In certain instances, the soil-cement mixture is

temporarily stored for several days before being transported and compacted at the designated site. This method helps optimize the use of space while supporting infrastructure development.

Ayeldeen et al. (2016) reported that noted that the chemical reaction of cement begins immediately upon mixing with soft soil, causing the mixture to start gaining strength. Disturbing the mixture several days after mixing can impact its strength; however, the soil-cement mixture is still capable of gaining additional strength even after being disturbed, transported, and compacted.

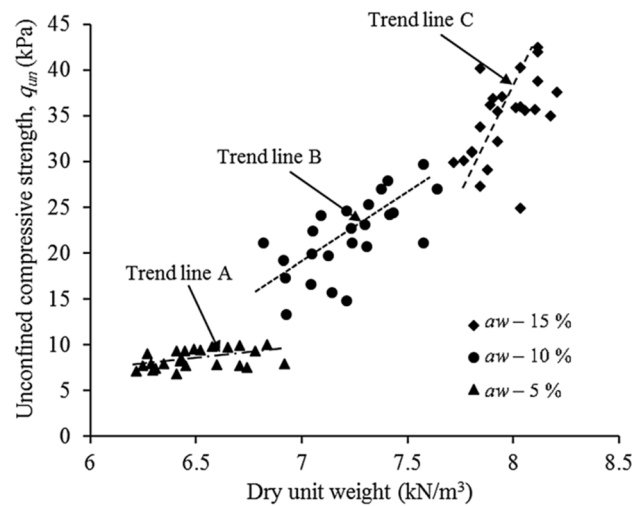


Figure 1 Relationship between dry unit weight and disturbed unconfined compressive strength (Ayeldeen et al., 2016)

Figure 1 illustrates the relationship between dry unit weight and disturbed unconfined compressive strength for various cement ratios (5%, 10%, and 15%). This relationship is clearly influenced by the cement content, as seen in the varying slopes of the three trend lines (A, B, and C). The slope of trend line A is nearly horizontal, indicating that changes in dry unit weight have little effect on strength. In contrast, the slopes of trend lines B and C are steeper, with slope C being the steepest. These findings suggest that both cement content and compaction energy

play a significant role in improving the dry unit weight and unconfined compressive strength of disturbed soil, even after several days from mixing.

In addition to compaction performance, the permeability (k) of cement-stabilized clay has also been widely studied, with several researchers examining the effects of lime and cement improves the permeability of soil (McCallister & Petry, 1992; Al-Mukhtar et al., 2012; Quang & Chai, 2015). These studies indicate that the a key factor of permeability in soil is pore distribution. When the cement or lime content are more than 3%-4% by dry weight, the cementation products formed, and fill the pore space within soil specimen, leading to a reduction in the permeability.

It is evident that the addition of cement or stabilizers can enhance the mechanical properties of clay. However, considering the imperative of cost-effective construction and advancing the principles of 3Rs, emphasizing recycled materials, alternative options like recycled concrete aggregate from C&D waste are being explored.

2.2 Recycled Concrete Aggregate and Application

The growing prevalence of urban construction and renewal projects in both developing and developed countries has led to a continuous rise in construction and demolition (C&D) waste being sent to landfills. Recycling and reusing C&D materials in applications like pavement construction helps conserve natural resources and reduce environmental pollution. Recycled concrete aggregate (RCA), a common form of C&D waste generated during the construction, renovation, or demolition of buildings, roads, and bridges, can exhibit different performance characteristics compared to other aggregates due to the variability in properties within the individual RCA particles.

2.2.1 Density, Porosity, and Water Absorption

The density, porosity and water absorption of RCA are primarily influenced by the residual mortar adhered to the aggregates. This residual mortar affects the physical properties of the RCA, making it different from natural aggregates in terms of its overall structure and behavior. Limbachiya et al. (2000) reported that the relative density of RCA is lower than natural aggregate (NA) about 7-9%. This is also aligned well with Sagoe-Crentsil et al. (2001) represented the difference of density between RCA and NA about 17% with bulk densities of 2.89 kg/m^3 . This is because RCA is a highly porous material with greater contaminant content (Agrela et al., 2012). Its lower density is due to the adhered mortar, which is lighter than natural aggregates (NA) of the same volume. Higher porosity makes RCA more water-absorbent than NA, with water absorption rates of around 4–4.7% under saturated conditions, compared to 0.5–1% for NA (Shayan & Xu, 2003). (Shayan & Xu, 2003).

2.2.2 Hydraulic Performance of RCA-Reinforced Clay Mixtures

Al-Moadhen et al. (2018) studied the hydraulic conductivity of composite soils, finding that it is influenced with several factors such as clay content, clay type, and void ratio. In matrix-dominated soils ($\geq 35\%$ fines), flow is controlled by the matrix void ratio and clay type, whereas in clast-dominated soils ($\leq 20\%$ fines), it depends on the intergranular void ratio and particle size distribution. For soils with 20–35% fines, flow behavior is influenced by confining pressure and density.

Shaker and Elkady (2015) conducted a study on determining the optimal coarse gravel content for achieving the lowest hydraulic conductivity in compacted soil liners. Their research found that gravel contents below 60% have minimal impact on hydraulic conductivity, as all test specimens showed low values. However, when gravel content exceeds 50–60%, voids between gravel particles remain unfilled by clayey soil, increasing hydraulic conductivity. The moisture content of the non-gravel fraction proved to be a reliable indicator for achieving optimal

compaction conditions. Controlled experiments on molding water content, compaction energy, and gravel-soil mixing suggest that the maximum content of gravel is approximately 50%.

Tavakoli et al. (2010) investigated clay mixed with aggregates, as core material for embankment dams and nuclear waste disposal backfill, highlighting the significance of understanding the hydraulic conductivity of composite clay. Their tests showed that hydraulic conductivity decreases as aggregate content increases up to 40%, after which further addition of aggregates leads to an increase in hydraulic conductivity, as depicted in Figure 2.

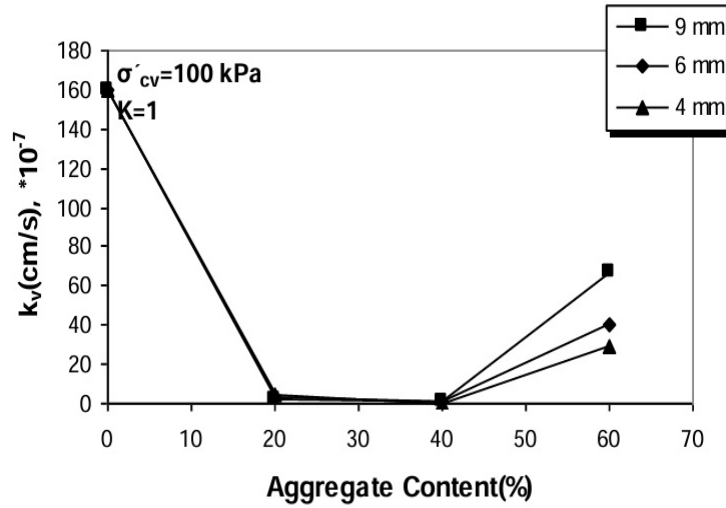


Figure 2 Effect of coarse aggregate content on the hydraulic conductivity (Tavakoli et al., 2010)

2.2.3 Evolution Mechanism and Internal Structure within RCA-Reinforced Clay Mixtures

Based on previous research, hydraulic conductivity of clay-aggregate mixtures decreases as aggregate content increases, likely due to the formation of a heterogeneous hydraulic conductivity field within the clayey matrix (Tavakoli et al., 2010).

Lu et al. (2021) found that the inclusion of aggregates in compacted clay-coarse aggregate mixtures creates a heterogeneous density field. During compaction, clay fractions between coarse aggregates consolidate under higher confining stress, becoming stiffer and denser than the surrounding clay. These denser clayey bridges form network structures around

the aggregates, enhancing stability and reducing permeability due to the lower void ratio in the clay matrix, as shown in Figure 3.

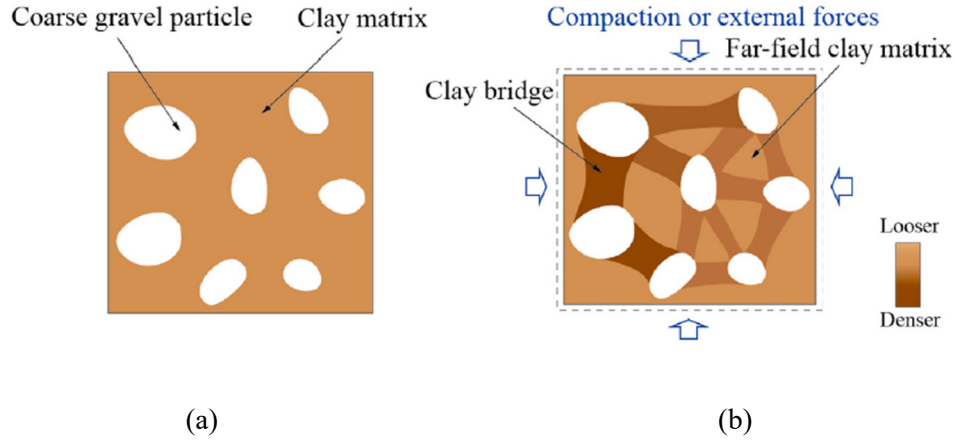


Figure 3 Schematic diagram of density field developed in a coarse aggregate-clay mixture (a) before and (b) after compaction or external forces (Lu et al., 2021)

Based on soil mechanics, a smaller total void ratio indicates a denser state and lower permeability for homogeneous soils. However, previous research on the hydraulic performance of RCA or coarse aggregate contents indicates that the hydraulic conductivity of composite soil consisting of RCA and clay sharply increases when the aggregate content exceeds 40-50%.

Lu et al. (2021) studied the internal structure of RCA-reinforced clay mixtures. They found that adding RCA materials significantly inhomogenizes the internal structure, making macro permeability behavior dependent not only on compactability but also on the meso-structure of RCA-clay distributions. Even though the total void ratio of RCA-clay mixtures decreases as RCA content increases, the permeability might be controlled more by the clay matrix void ratio than by the total void ratio. Lu et al. (2021) provided the following Equation (1) and (2) to calculate the clay matrix void ratio:

$$e_c = \frac{G_c}{\rho_{dc}} - 1 \quad (1)$$

$$\rho_{d_c} = \frac{G_c \times \rho_{d_m} \times (1 - C_g)}{G_g - \rho_{d_m} \times C_g} \quad (2)$$

where e_c is the void ratio of clay matrix; ρ_{d_m} and ρ_{d_c} is dry density of mixtures and clay matrix (M/L³); G_c G_g is the specific gravity of coarse aggregate and C_g is coarse aggregate content. Figure 4 illustrates the void ratio and density of the clay matrix change with increasing coarse aggregate content. Up to 30%, the matrix densifies with minimal void ratio change, reducing permeability. Beyond this, gravel isolates the matrix, raising the void ratio and lowering density, shifting the structure from gravel-suspension to gravel-contact, which increases permeability. Thus, total void ratio alone may not reliably indicate permeability in composite soils, as it overlooks the matrix's role in sandy clay and intergranular structure in clayey sands (Al-Moadhen et al., 2018).

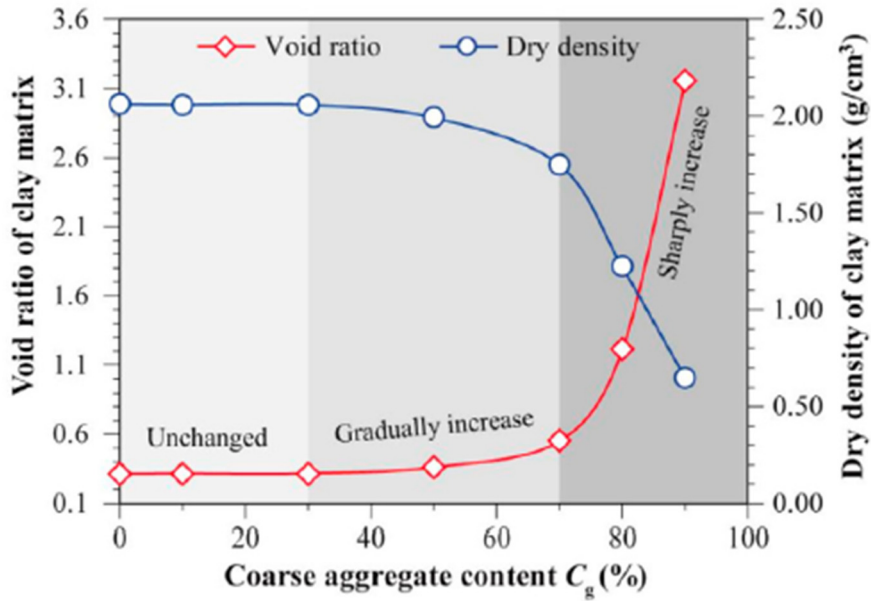
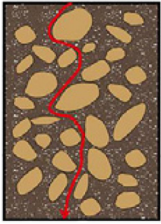
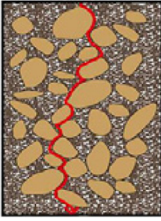
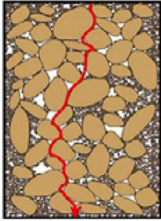


Figure 4 Void ratio and dry density of clay matrix in coarse aggregate-clay mixtures of different coarse aggregate contents (Lu et al., 2021)

Furthermore, Lu et al. (2021) identified potential preferential flow paths in composite soil based on varying meso-structures and clay matrix void ratios, as shown in Table 1. While

cement-stabilized clay and coarse aggregate reinforcement improve soil mechanical properties and support material recycling, they also raise environmental concerns due to hexavalent chromium (Cr(VI)) in cementitious materials. Thus, a thorough understanding of Cr(VI) leaching behavior and compliance with Japanese environmental standards is crucial.

Table 1 Idealized preferential flow paths and dominate occurrence conditions in the tested coarse aggregate-clay composite samples (Lu et al., 2021)

Type	Diagram	Percentage of Cg (%)	Descriptions
i		$C_g < 30\%$	Seepage mainly occurs through the compacted clay matrix when coarse aggregate content is low, with permeability primarily controlled by the clay matrix's void ratio.
ii		$C_g < 30\%$	Seepage flows around the gravel aggregate due to its impermeability. Increasing a small amount of gravel lengthens flow paths within the dense clay matrix, leading to a slight reduction in permeability.
iii		$30\% < C_g < 50\%$	Seepage occurs at the clay-aggregate interface, where weak bonding often significantly reduces permeability.
iv		$C_g > 50\%$	At high gravel content, numerous inter-particle voids form as the clay matrix becomes fully separated by the gravel skeleton, significantly increasing permeability.

2.2.4 Mechanical Performance of RCA-Reinforced Clay Mixtures

Recycled concrete aggregate (RCA) has significant potential for reuse, with numerous studies exploring its application in concrete, mortar, and road construction.

Kianimehr et al. (2019) assessed RCA's impact on the shear and compressive strength of clay soils, finding that RCA increases unconfined compressive strength (UCS) and enhances shear strength, particularly with moist curing. RCA-clay blends exhibit greater stiffness, reduced compressibility, and dilative behavior, making them suitable for pavement layers such as base, subbase, and subgrade.

Lu et al. (2021) investigated the incorporation of RCA into clay-based impervious cores to assess its impact on compaction performance. Figure 5 showed that the highest value of global dry density is attained with 70% RCA content in the clay mixture. However, for cases where the coarse aggregate content exceeds 70%, overall dry density shows no significant variation with changes in RCA. The compaction curves remain relatively unchanged, similar to previous research (Mitchell & Soga, 2005). These compaction test results indicate a critical transition in coarse aggregate content, where the compaction behavior changes from that of clayey soil to that of coarse cohesionless soil.

Shourijeh et al. (2022) highlight the potential of RCA and fiber reinforcement in soil stabilization, offering an environmentally friendly alternative to conventional materials. Figure 6 showed that the strength of improved clay with 0.5% fiber and 10% RCA achieved the strength requirements for pavement subbase after 28 days of curing.

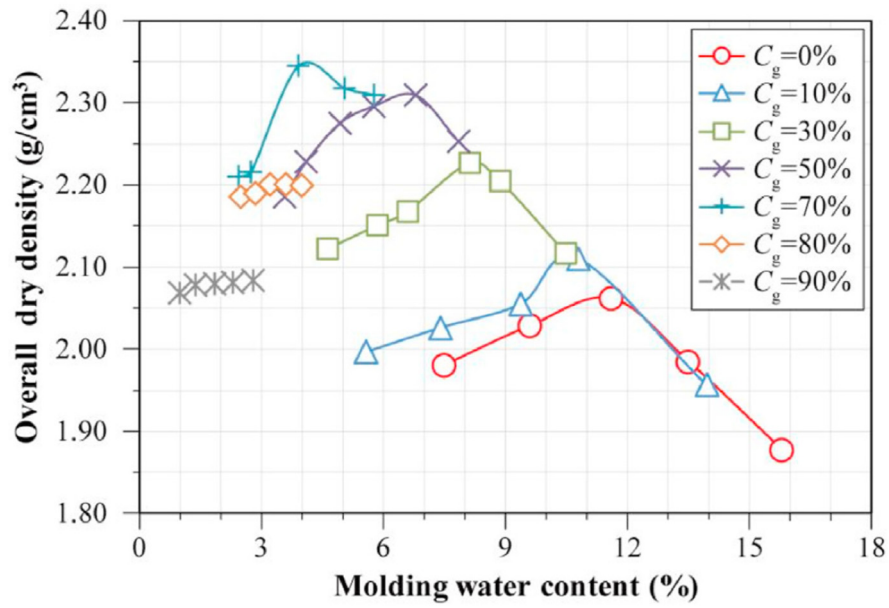


Figure 5 Compaction curves with different RCA contents (Lu et al., 2021)

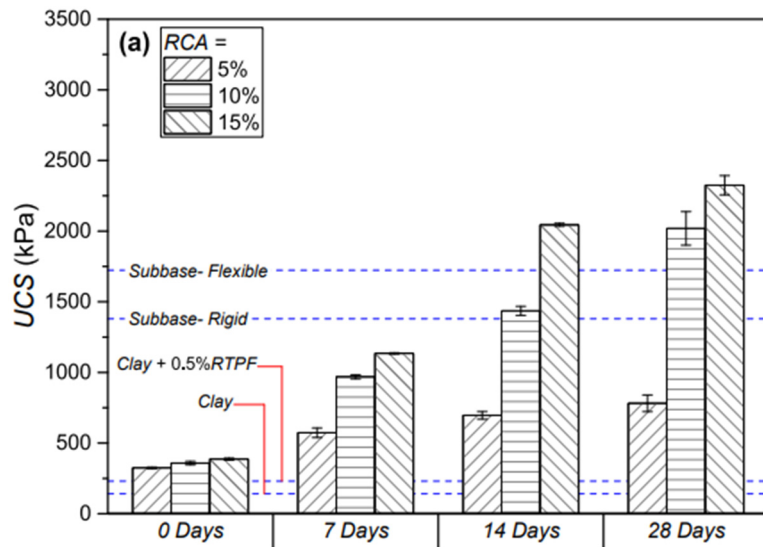


Figure 6 The UCS test of clay-fiber-RCA composites (Shourijeh et al., 2022)

RCA is recognized as a promising material for sustainable construction. Research on its sustainable use is crucial and will remain vital for future development. However, existing literature has mainly concentrated on the mechanical performance of stabilized clay with coarse aggregates. In dam or landfill engineering, not only mechanical behavior, such as bearing capacity and compaction performance, but also permeability characteristics, play a critical role in engineering safety. Several influential factors on soil permeability are investigated, such as porosity (Yuan et al., 2019). However, when RCA is added to soil, the internal structure within the specimen between RCA and soil undergoes transformation, resulting in inhomogeneity. As a result, permeability is influenced not only by the dry density and total porosity values of RCA-soil specimens (Al-Moadhen et al., 2018) but also by the meso-structure distribution of RCA-soil.

2.3 Chromium in the Environment

Chromium exists in trivalent (Cr(III)) and hexavalent (Cr(VI)) forms, with Cr(III) serving as a beneficial trace metal in metabolism (Kośła et al., 2019), while Cr(VI) is highly toxic, carcinogenic, and harmful to aquatic life. Cr(III) forms stable complexes in water and precipitates as hydroxides at pH 5.5–6.5 (Lydersen et al., 2002). In contrast, Cr(VI) exists as mobile oxyanions, persisting in low-organic water and reducing to Cr(III) through reactions with organic matter, Fe(II), or sulphides (Steven et al., 1976). Oxidation of Cr(III) to Cr(VI) is limited, primarily facilitated by oxygen and manganese oxides (Rai et al., 1989)..

2.4 Hexavalent Chromium (Cr(VI)) Leaching from Cementitious Materials

Cement-based secondary materials like RCA and cement contain hexavalent chromium (Cr(VI)) because Cr(III) in raw materials such as clay and limestone, used in cement manufacturing, can be oxidized to Cr(VI) during the production process.

Calcium hydroxide (Ca(OH)_2) from RCA and Cement result to alkalinity in the water ($\text{pH} = 12.35$). In this alkalinity condition Cr(III) and Cr(VI) build as Cr(OH)^{4-} and CrO_4^{2-} , respectively. The alkalinity of RCA and cement, driven by Ca(OH)_2 , results in a pH of 12.35. In such conditions, Cr(III) and Cr(VI) exist as Cr(OH)^{4-} and CrO_4^{2-} , respectively. While Cr(OH)_4 can leach in high concentrations, Cr(OH)^{4-} remains low due to its equilibrium with insoluble Ca-Cr(III) minerals.(Cornelis et al., 2008). However, leaching of Cr(VI) from these materials could pose an environmental threat, potentially harming ecosystems and human health (Frías et al., 1994).

In case of RCA and SS are employed as a geotechnical material for soil improvement, it could lead to contaminated soil. The primary concern from a geo-environmental perspective is the leaching of heavy metal contaminants from those materials into the ground via groundwater flow. According to ministry of environment in Japan enacted the Soil Contamination Countermeasure in 2003, the agency notification No.46 designated the 27 substance as heavy metal contaminated substances. (See Table 2). Considering of environmental impacts of Cr(VI), in 2022, the environmental standard for Cr(VI) concentration in groundwater has been reduced from 0.05 to 0.02 (ML^{-3}). Considering these concerns, it is imperative to explore the leaching characteristics of Cr(VI) from RCA and SS when employed as a geotechnical material for soil improvement purposes.

Table 2 Designated contaminated substances in Japanese law

Contaminated substance	Allowable concentration (ML ⁻³)
Cadmium	< 0.003
Total Cyan	_*
Organic phosphorus	_*
Lead	< 0.01
Hexavalent chromium	< 0.02
Arsenic	< 0.01
Total mercury	< 0.0005
Alkyl mercury	_*
Polychlorinated biphenyl	_*
Dichloromethane	< 0.02
Carbon tetrachloride	< 0.002
Chloroethylene	< 0.002
1,2-Dichloroethane	< 0.004
1,1-Dichloroethylene	< 0.1
1,2-Dichloroethylene	< 0.04
1,1,1-Trichloroethane	< 1
1,1,2-Trichloroethane	< 0.006
Trichloroethylene	< 0.01
Tetrachloroethylene	< 0.01
1,3-Dichloropropene	< 0.002
Chlulam	< 0.006
Simazine	< 0.003
Thiobencarb	< 0.02
Benzene	< 0.01
Selenium	< 0.01
Fluorine	< 0.8
Boron	< 1
1,4-Dioxane	< 0.05

_* is undetectable during sample solution

2.5 Influencing Factors on Cr(VI) Concentration from Cement-Stabilized Soil

In addition, understanding the influencing factors on leaching of Cr(VI) from cement or secondary cementitious materials for soil improvement is also important to minimize the environmental risks and achieve environmental suitability. the leaching of Cr(VI) is influenced by several factors such as field conditions, temperature, leaching test standard and technical methods.

Inui et al. (2008) developed a framework to assess contaminant leaching from recycled concrete aggregates in geotechnical applications. While regulatory leaching tests characterize the leaching potential of contaminants, they may not accurately predict actual leaching behavior under field conditions. This study examined the effect of grain size on leaching by conducting batch tests following Japanese environmental agency notification No. 46 (JLT46) on samples with particle sizes of 19 mm, 13.2 mm, and 2 mm. Figure 7 shows the concentration of different particle sizes provide different Cr(VI) concentrations. The leaching concentrations of under 2 mm sample are the higher than those of RCA. Inui et al. (2008) suggested that RCA crushed to under 2 mm, following the JLT46 standard, may lead to an overestimation of Cr(VI) concentration compared to RCA in its original form. Additionally, this study examined acceleration tests that simulate real-world conditions, including wetting-drying, freezing-thawing, and abrasion tests with various sample forms.

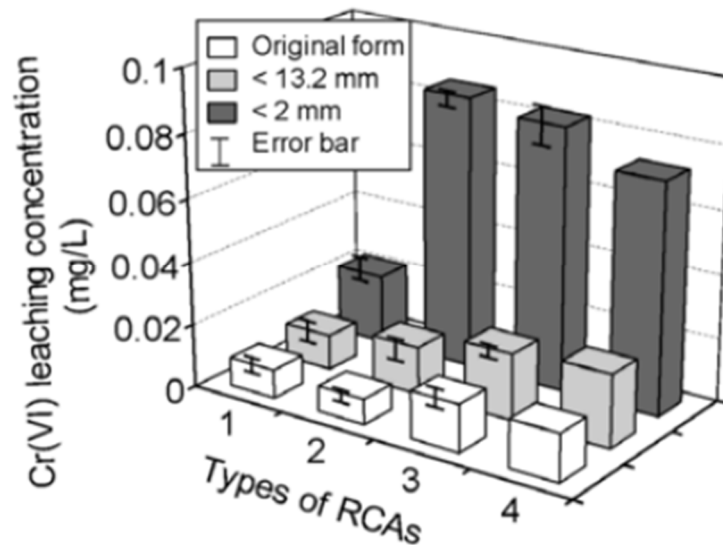


Figure 7 Cr(VI) leaching concentration in the batch leaching tests (Inui et al., 2008)

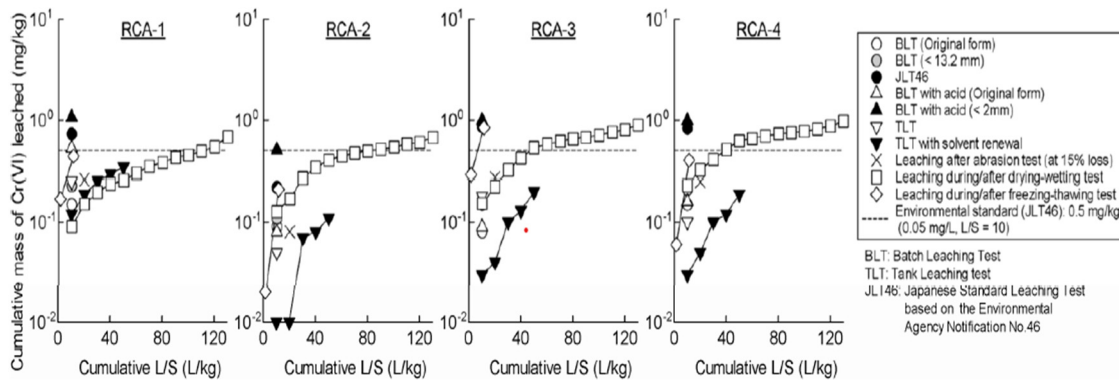


Figure 8 Comparison of Cr(VI) leaching amounts obtained in various testing methods (Inui et al., 2008)

Figure 8 illustrates that exposure to accelerated conditions—wetting-drying, freezing-thawing, and abrasion—increased Cr(VI) leaching from RCA, with wetting-drying having the most significant effect. For RCA with substantial surface mortar, freezing-thawing also notably enhanced leaching. However, the Cr(VI) leaching from granular RCA under these conditions did not exceed that observed in conventional batch tests conducted on crushed RCA (<2 mm).

Chai et al. (2009) investigated the Cr(VI) concentration from fly ashes with additives in leachate influenced by several factors with different testing methods (batch and tank leaching test) as shown in Figure 9a. Ideally, the solid/liquid contact area for the tank leaching test, which is in compacted form, is less than that of the corresponding batch contact test conducted for crushed samples under 2 mm, which may result in lower Cr(VI) concentration. In addition, this research also observed the effect of curing time and clay on leaching of Cr(VI) concentration. Curing significantly reduced Cr(VI) concentration, with the greatest effect observed within the first week (Figure 9b), likely due to cementation. This mechanism aligns with the stabilization/solidification (S/S) method for treating contaminated soil. Chai et al. (2009) noted that allowing over a week of curing for fly ash-cement embankments minimizes environmental risks from rainfall exposure.

It should be noted that, in the environment, Cr(VI) is mainly present as chromate (CrO_4^{2-}), hydrogen chromate (HCrO_4^-) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) (Estokova et al., 2018). In S/S method, the Cr(VI) was performed as CrO_4^{2-} because the pH of cement was greater than 12 in cement hydration condition (Chai et al., 2009) as shown in Figure 10.

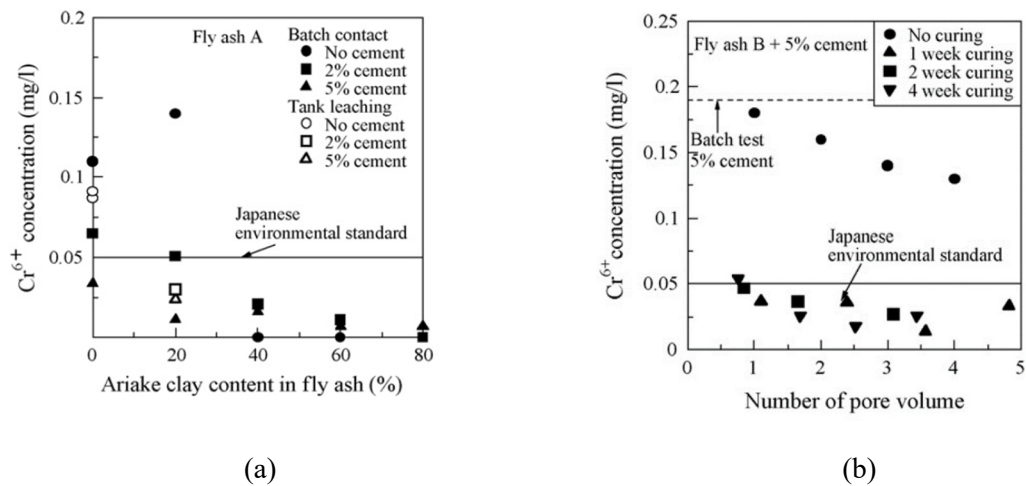


Figure 9 Effect factors on Cr(VI) concentration; a) effect of leaching test standard; b) effect of curing time (Chai et al., 2009)

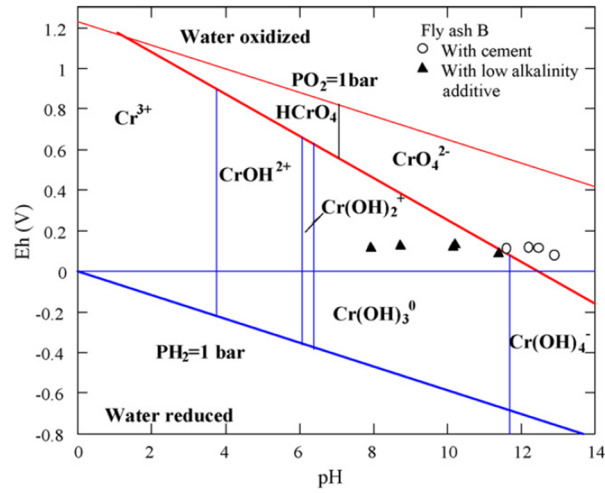


Figure 10 Eh–pH diagram for chromium and batch test results of fly ash (Chai et al., 2009)

Wang and Vipulanandan (2000) studied the effect of cementation on Cr(VI) concentration through X-ray diffraction (XRD). The XRD results for cement with different concentrations of Cr(VI) in the cement. The possible between Cr(VI) and cement can be report as Equation (3)



Figure 11 presents the X-ray diffraction (XRD) results, showing a decrease in Ca(OH)_2 intensity in the Cr(VI)-containing sample. This reduction suggests that Ca^{2+} reacted with CrO_4^{2-} , which in turn delayed cement setting.

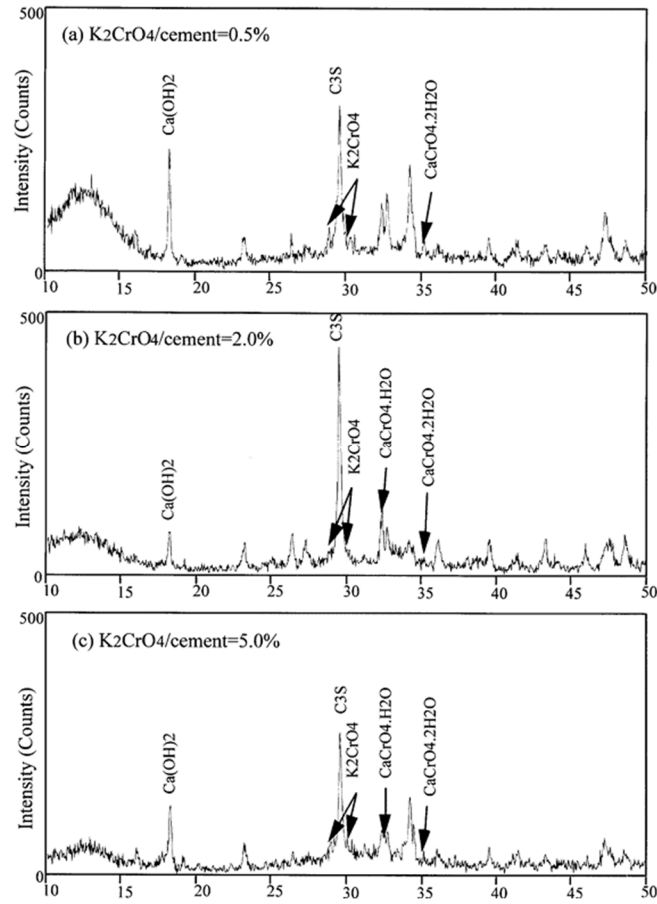


Figure 11 XRD pattern of reaction between Cr(VI) and cement (Wang and Vipulanandan, 2000)

Besides the CaCrO_4 dissociated and reacted with the hydrogen ion according to Equation (3). The reaction of Equation (4) explains the recovery of Cr(VI).



2.6 Contaminant Transport through Porous Media

A solution is a mixture where substances are fully dispersed, with the solvent dissolving the solute. Solute transport refers to the movement of dissolved contaminants in saturated porous media. This research focuses on the transport mechanisms of these contaminants, including advection, dispersion, diffusion and adsorption.

2.6.1 Advection

Advective transport for contaminant migration is driven by a hydraulic gradient (Sharma & Reddy, 2004). For one-dimensional steady-state flow, groundwater seepage velocity can be expressed using Darcy's law (Booker et al., 2004) as the following Equation (5).

$$v = \frac{ki}{n_e} \quad (5)$$

where v is average transport velocity (LT^{-1}); k is the hydraulic conductivity (LT^{-1}); n_e is the effective porosity (-), and i is the hydraulic gradient (-). Effective porosity is the portion of void space that contributes to flow, as not all voids conduct flow, making it always equal to or less than total porosity. The one-dimensional steady-state mass flux of a contaminant transported by advection is given by Equation 6.

$$\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} \quad (6)$$

where $\frac{\partial c}{\partial t}$ is the advective mass flux ($ML^{-3}T^{-1}$); c is concentration (ML^{-3}); t is time (T); x is direction of flow (L) and $\frac{\partial c}{\partial x}$ is concentration gradient (ML^{-4}).

2.6.2 Dispersion

The hydrodynamic dispersion coefficient, D is the sum of effective diffusion coefficient, D_{eff} (L^2/T) and mechanical dispersion coefficients, D_{md} (L^2/T). This relationship is expressed as follows (see Equation (7)-(8)) (Freeze & Cherry, 1979);

$$D_{md} = \alpha v \quad (7)$$

$$D = D_{eff} + D_{md} \quad (8)$$

where α is dispersity (L) and v is seepage velocity (L/T)

For contaminant transport through porous media at low velocities, the dispersion coefficient simplifies to D^* (i.e. $D \approx D^*$). As the seepage velocity surpasses the material's yielding velocity, the dispersion coefficient increases in proportion to the velocity. The influence of velocity on mixing is captured by D_{md} .

2.6.3 Diffusion

Diffusion describes the contaminant migration is driven by a concentration gradient. According to Fick's first law (Equation (9)) described in steady-state diffusion where the concentration gradient does not change with time (Shackelford & Daniel, 1991b).

$$J_d = D_0 \frac{\partial c}{\partial x} \quad (9)$$

where J_d is the diffusive mass flux ($\text{ML}^{-2}\text{T}^{-1}$), D_0 is Molecular diffusivity (L^2T^{-1}). D_0 , represents the maximum diffusion rate of a species under ideal conditions, such as in pure water at infinite dilution on a microscopic scale. In non-ideal conditions, factors like electroneutrality, solute-solute, and solute-solvent interactions influence diffusion, especially in concentrated solutions and macroscopic systems (Shackelford & Daniel, 1991a).

When diffusion occurs in porous media, contaminants follow tortuous and irregular paths rather than moving in a straight line (Rowe et al. 2004). Since these pathways are tortuous to measure directly, tortuosity (τ) is determined indirectly as a factor influencing diffusion. Though often considered a form of physical retardation inherent to the solid matrix. Tortuosity is the ratio of the actual winding path of diffusion to the straight-line distance between two points. However, measured tortuosity values also account for factors such as fluidity changes and electrostatic interactions with solid particles. The effective diffusion coefficient, D_{eff} , is related to D_0 by τ , as shown in Equation (10) (Rowe et al. 2004);

$$D_{eff} = \tau D_0 \quad (10)$$

Fick's first law may be used to describe the diffusive mass flux, J_d ($\text{ML}^{-2}\text{T}^{-1}$) through porous media (Equation (11));

$$J_d = -n_e D_{eff} \frac{\partial c}{\partial x} \quad (11)$$

where n_e is the effective porosity. The negative sign in Equation (9) is necessary because, by convention, $\frac{\partial c}{\partial x}$ is negative. Fick's second law (Equation (12)) describes how diffusion leads to changes in concentration over time.

$$\frac{\partial c}{\partial t} = \frac{D_{eff}}{R_d} \frac{\partial^2 c}{\partial x^2} = D^{app} \frac{\partial^2 c}{\partial x^2} \quad (12)$$

where R_d is retardation factor and D^{app} ($D^{app} = D^*/R_d$) is apparent diffusion coefficient (L^2T^{-1}).

Retardation factors can reflect the ability to impede contaminant migration. The high R_d values indicate a high sorption capacity of the solid, primarily through processes such as adsorption, ion exchange. The R_d can be calculated as Equation (13);

$$R_d = 1 + \left(\frac{\rho_{dm} \times K_d}{n} \right) \quad (13)$$

where ρ_{dm} is the total dry density of mixture (M/L^3); n is porosity of soil and K_d is partitioning coefficient.

2.6.4 Sorption

Sorption, a critical process in groundwater, removes contaminants through mechanisms like absorption, adsorption, precipitation, and ion exchange. Absorption incorporates contaminants into a solid's interior, while adsorption binds them to its surface. Precipitation transforms dissolved species into solids, and ion exchange swaps ions between the solution and solid. These processes often overlap but collectively reduce solute concentrations.

In many studies related to clayey barriers, the term "adsorption" is commonly used instead of sorption. The process by which a contaminant shifts from the solution to the solid phase, or vice versa, is referred to as partitioning or distribution. This relationship is often described by the partitioning coefficient, K_d ($M^{-1}L^3$). In most cases, the adsorption of a given solute is often characterized using an adsorption isotherm. The Henry isotherm is usually adopted to calculate the K_d as following Equation (14);

$$q = K_d C_r \quad (14)$$

Where q is the adsorption capacity in solidified contaminated soil (MM^{-1}), C_r is the concentration of solute (ML^{-3}), and M_T is the total mass of substances involved in the adsorption equilibrium (MM^{-1}). This simple model is often suitable for low concentrations or high sorbent intake, where the relationship between q and C_r is approximately linear. At high concentrations, adsorption is nonlinear, typically modeled by Freundlich or Langmuir isotherms, which can be linearized for regression analysis to determine curve-fitting parameters. The Freundlich isotherm is given by Equation (15);

$$q = K_d C_r^\varepsilon \quad (15)$$

where ε is an empirically determined constant. The Freundlich model represents a power equation and reduces to Equation (14) for $\varepsilon = 1$.

2.7 One-Dimensional Contaminant Transport Equation

The combination of advection, diffusion, dispersion, and sorption mechanisms yields the transient equation for one-dimensional contaminant transport through intact porous material, as shown in Equation (16) (Rowe et al. 2004).

$$n_e \frac{\partial c}{\partial t} = n_e D_{eff} \frac{\partial^2 c}{\partial x^2} - n_e v \frac{\partial c}{\partial x} - \rho_{dm} K_d \frac{\partial c}{\partial t} \quad (16)$$

Equation 16 is rearranged to the form shown in Equation (17);

$$R_d \frac{\partial c}{\partial t} = D_{eff} \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (17)$$

2.8 Determination of Partitioning Coefficient and Apparent Diffusion Coefficient

2.8.1 Batch Leaching Test

The K_d in Equation (14) can be evaluated using a batch leaching test, which examines solute adsorption onto materials such as clayey soil. This process involves agitating a mixture of soil and chemical solution in a specific ratio for 24 hours at a controlled temperature of 25°C. Solute concentrations are measured before mixing (C_o) and after equilibrium (C_r). The adsorbed concentration (q) is calculated using the following Equation (18);

$$q = \frac{(C_o - C_r)V}{m} \quad (18)$$

where V is volume of solution (L^3) and m is solid mass (M). Repeating this process with varying initial solute concentrations produces adsorption isotherms, plotting the adsorbed concentration against equilibrium concentration. However, for potentially contaminant-releasing materials (PCMs) like dredged sludge, cement, and RCA, conventional batch leaching tests cannot determine these parameters.

2.8.2 L/S-Parallel Leaching Test

Sakanakura et al. (2021) developed the LS-parallel test to determine adsorption parameters for PCMs through parallel batch tests with varying liquid-solid ratios (1–300 L/kg). Conducted on sandy soil from marine sediment, the test examined contaminant kinetics and equilibrium over water-contact times of 10 minutes to 28 days. Adsorption parameters were successfully determined under adsorption-controlled conditions.

Ad/desorption parameters were calculated from leached concentrations in L/S parallel leaching tests. The Henry isotherm model was used to describe contaminant adsorption in the solid phase (see Equation (14)). ThFor replacing entiree total mass of the chemicals of concern

(COCs) involved in adsorption equilibrium, M_T (MM^{-1}), can be indicated as the combined amount the COCs adsorbed on the solid surface and leached mass of the COCs in liquid phase, as presented by Equation (19). With combination between Equations (14) and (19), Equation (20) can be obtained by fitting with linear regression between C_r and M_L , which M_L can be determined by Equation (21), then the slope represents the K_d while the interception represents the M_T , as shown in Figure 12. A higher K_d value indicates a greater affinity of the COCs to the solid phase, implying a reduced likelihood of leaching. Conversely, a higher M_T value suggests increased involvement of the COCs in ad/desorption reactions, indicating a higher potential for leaching compared to soils with smaller M_T .

$$q + M_L = M_T \quad (19)$$

$$M_L = M_T - K_d C_r \quad (20)$$

$$M_L = C_r \times L/S \quad (21)$$

where M_L is the leached mass of the COCs with different L/S (mg/kg)

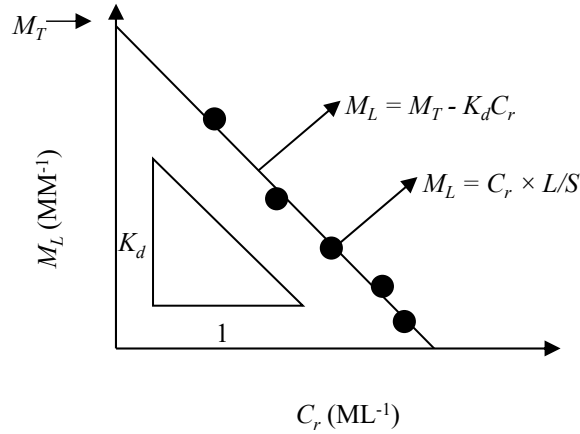


Figure 12 Relationship between M_L and C_r following Henry isotherm

2.8.3 Tank Leaching Tests

In order to determine the D^{app} , the cumulative mass released must be measured during the leaching tests. There are many leaching tests in Japanese standard, one of those leaching tests is tank leaching test (TLT). This test involves immersing a solid specimen in the solution

for 28 days (Ministry of Construction (Currently the Ministry of Land, 2000) as shown in Figure 13a. However, some of previous research conducted TLT with replacing entire solution. For each cumulative leaching interval, the entire solution was replaced, and solute concentrations were measured in each liquid fraction (see Figure 13b). This approach captures leaching driven by diffusion from the solid phase, enabling the determination of D^{app} .

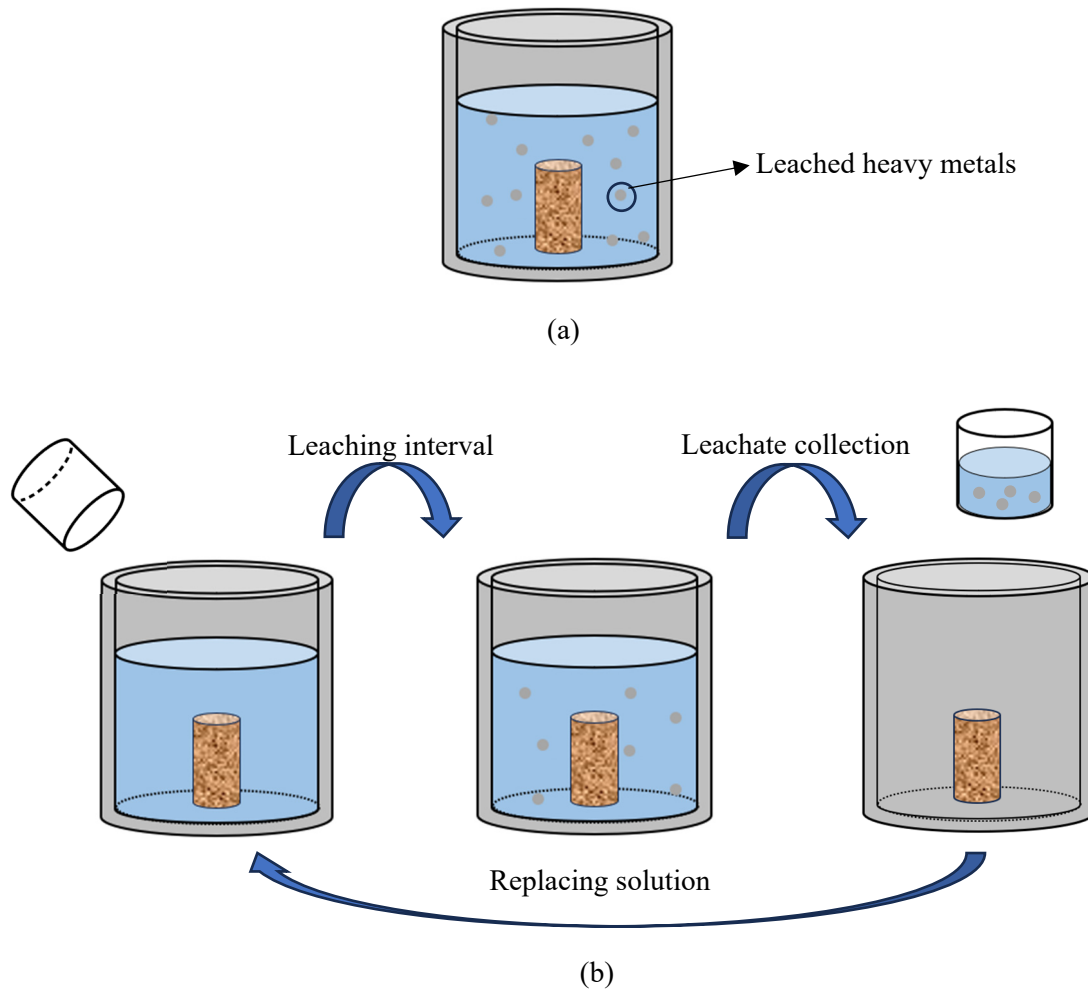


Figure 13 Schematic of TLTs; a) without the renewal solution for 28 days and b) with renewal solution with cumulative leaching interval time

In accordance with Fick's second law and its boundary conditions ($C(x=0, t) = 0$ and $C(x=\infty, t) = C_0$), alongside the initial condition ($C(x, t=0) = C_0$), where C is the concentration

for given time and C_0 is the initial concentration in porewater, the cumulative mass released of the COCs is represented by Equation (22) (Sample-Lord & Shackelford, 2016).

$$M_A = 2\rho_{dm} C_{av} \left(\frac{D^{app} t}{\pi} \right)^{0.5} \quad (22)$$

where M_A is the cumulative mass released of the COCs (ML^{-2}), C_{av} is available leaching concentration of the COCs in the mass of solid particles of specimens (MM^{-1}) which can be obtained from availability test, t is the cumulative leaching time (T). Applying the logarithm function to Equation (23) yields the following:

$$\log M_A = \log \left[2\rho_{dm} C_{av} \left(\frac{D^{app}}{\pi} \right)^{0.5} \right] + 0.5 \log t \quad (23)$$

The linear regression analysis was employed to estimate the leaching mechanism of the COCs by plotting the cumulative mass released of the COCs against cumulative leaching time using a logarithmic function. The slope obtained from the plots categorizes the leaching mechanism: a slope within the range of 0.35-0.65 indicates control by diffusion, a slope < 0.35 suggests control by surface wash-off, and a slope > 0.65 indicates control by dissolution (de Groot & van der Sloot, 1992). M_A was calculated as the cumulative sum of M_i , (ML^{-2}), representing the mass released of the COCs during the current leaching interval i , as shown in Equation (24);

$$M_i = \frac{C_i \times V_i}{A} \quad (24)$$

where C_i is the concentration of the COCs in leachate for each leaching interval i (ML^{-1}), V_i is the leachate volume for each leaching interval i (L^3), A is the surface area exposed to the leachate (L^2).

In case where the leaching mechanism is primarily governed by diffusion, the D_i^{app} can subsequently be calculated for each leaching interval using Equation (25);

$$D_i^{app} = \pi \left[\frac{M_i}{2\rho_{dm}C_{av}(\sqrt{t_i} - \sqrt{t_{i-1}})} \right]^2 \quad (25)$$

where D_i^{app} is the apparent diffusion coefficient of the COCs in leachate for each leaching interval i (L^2T^{-1}), t_i is the cumulative leaching time at the end of the current leaching interval (T), while t_{i-1} is the cumulative leaching time at the end of the previous leaching interval (T). Finally, the D^{app} was determined by taking average of the D_i^{app} values.

2.9 Significance of Diffusion on Migration of Chemicals through Porous Media

In low-advective flux porous media, like landfill liners and cement-based S/S waste forms, contaminant migration is mainly diffusion-driven. In fractured media, contaminants move faster through fractures, though matrix diffusion can still influence their transport. (Rowe et al., 2004). In fractured media, contaminants move faster through fractures, though matrix diffusion can still influence their transport.

Shackelford (2014) explains the role of diffusion in the migration of aqueous soluble chemicals through porous media using solute breakthrough curves (BTCs), which depict concentration changes over time at the effluent end of a column. As shown in Figure 14a, BTCs

are measured in the laboratory by: (1) establishing steady-state seepage conditions, (2) introducing a chemical solution with a known initial concentration (C_o) at the influent end, and (3) monitoring the effluent concentration ($C(L,t)$) over time (Shackelford & Redmond, 1995).

The BTC in Figure 14b, representing "advection plus mechanical dispersion," shows solute spreading mainly due to mechanical dispersion. When seepage velocity is low, diffusion remains influential. Compared to previous cases, this BTC shifts left, with a breakthrough time of 14.8 years at $C(L,t)/C_o = 0.5$, significantly shorter than the 21.8 years observed without diffusion. Ignoring diffusion in transport modeling could lead to inaccurate and overly high breakthrough time estimates.

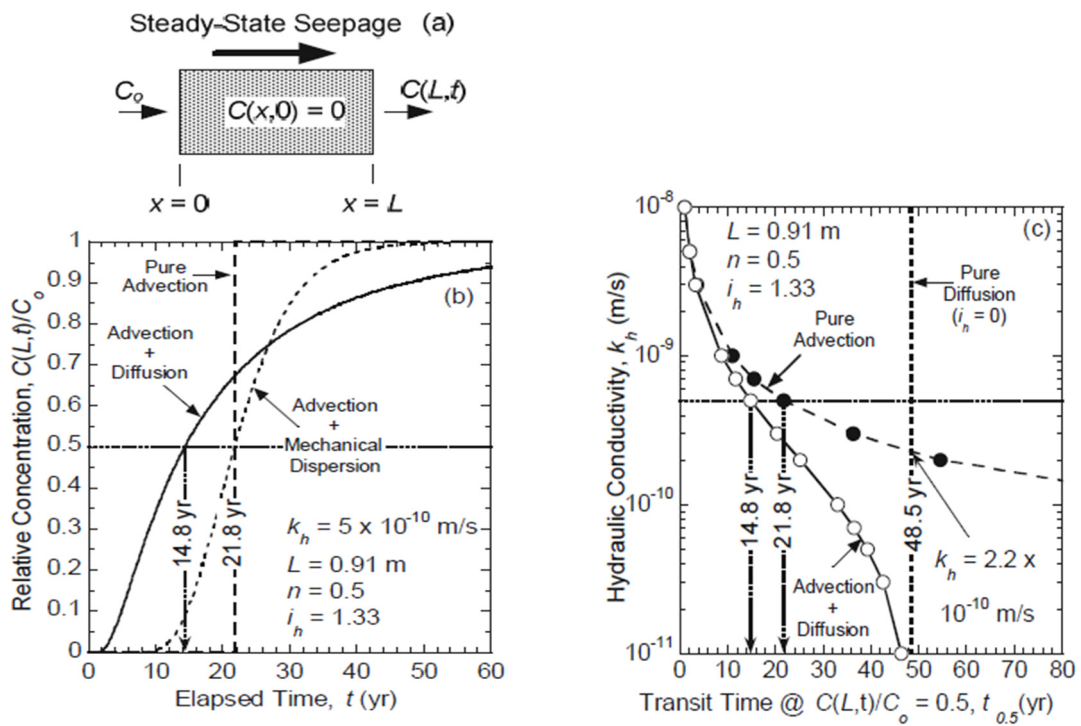


Figure 14 Effect of diffusion on solute transport through a column of soil of length, porosity and hydraulic conductivity (K) under a hydraulic gradient (i_h); a) column with porous medium; b)

Breakthrough curves illustrating diffusion effects at low K and c) Transit times ($t_{0.5}$) as a function of K (Shackelford, 2013).

Breakthrough time reduction due to diffusion depends on seepage velocity (v), as shown in Figure (14b). Figure (14c) illustrates breakthrough times at $C(L,t)/C_0 = 0.5$ ($t_{0.5}$) for pure advection and advection-diffusion under constant conditions, with hydraulic conductivity (K) as the variable. A pure diffusion case ($i_h = 0$) is also included for comparison. Key observations from Figure (14c) include:

- Diffusion influences breakthrough times even at $K = 10^{-9}$ (LT^{-1}), the regulatory limit for many waste containment applications.
- Predicting breakthrough times using only Darcy's law (pure advection) is highly unconservative for $K < 2.2 \times 10^{-2}$ (LT^{-1}).
- Diffusion dominates at $K \approx 2-3 \times 10^{-10}$ (LT^{-1}), as the advection-diffusion curve aligns with the pure diffusion curve.

This analysis underscores the need to account for diffusion in low-permeability media to ensure accurate contaminant transport predictions. Even at low K , solute mass flux can be environmentally significant, necessitating its inclusion in transport models.

2.10 Diffusion Coefficient for Cement-Based Materials

Diffusion significantly influences low-permeability porous media, prompting research on natural clays and clay barriers, including compacted clays, cementitious chemical barriers, and composite material barriers. While some studies have examined the leaching behavior of composite materials for specific mix designs, research on how varying mixture characteristics affect diffusion and porosity remains limited.

Composite materials, such as soil-cement or soil-coarse concrete aggregate mixtures, have distinct pore structures compared to concrete, cement mortars, and cement pastes. Despite expectations of different contaminant migration properties due to their composition, studies on similar materials provide valuable insights given the scarcity of data on soil-cement products. Diffusion in these materials is typically assessed using the effective diffusion coefficient, often referred to as the D^{app} in test procedures. Table 3 summarizes findings from various studies on cementitious materials.

Table 3 Effective diffusion coefficients for various stabilized soil with different standards

Element	D_{eff} (L^2T^{-1})	Binder/Material	Author	Test method
Pb	3.10E-13	Phosphate-clay binder	Wei et al. (2022)	USEPA 1315
Zn	7.00E-13	Phosphate-clay binder	Wei et al. (2022)	USEPA 1315
Cd	2.32E-10	Phosphate-clay binder	Wu et al., (2017)	USEPA 1315
As	5.45E-11	Fly ash (Class C)-soil	Moon and Dermatas (2007)	ANS 16.1
Pb	2.80E-10	Fly ash (Class C)-soil	Moon and Dermatas (2007)	ANS 16.1
Na ⁺	9.70E-12	Cement-Soil	Malviya and Chaudhary (2006)	NEN 7345
K ⁺	2.40E-11	Cement-Soil	Malviya and Chaudhary (2006)	NEN 7345
Cl ⁻	4.70E-11	Cement-Soil	Malviya and Chaudhary (2006)	NEN 7345
So ₄ ²⁻	3.30E-12	Cement-Soil	Malviya and Chaudhary (2006)	NEN 7345
Ca ²⁺	1.30E-13	Cement-Soil	Malviya and Chaudhary (2006)	NEN 7345
Pb ²⁺	1.10E-12	Cement-Soil	Malviya and Chaudhary (2006)	NEN 7345
Zn ²⁺	8.20E-15	Cement-Soil	Malviya and Chaudhary (2006)	NEN 7345
Fe ²⁺	4.30E-12	Cement-Soil	Malviya and Chaudhary (2006)	NEN 7345
Mn ²⁺	2.90E-12	Cement-Soil	Malviya and Chaudhary (2006)	NEN 7345
Cu ²⁺	9.70E-13	Cement-Soil	Malviya and Chaudhary (2006)	NEN 7345

Chapter 3: Investigation into the leaching of Cr(VI) from cement-stabilized soil and Influencing Factors

3.1 Introduction

The first chapter, a preliminary investigation into the leaching of Cr(VI) from cement-stabilized soil. Additionally, it examines the factors influencing Cr(VI) concentration, such as specific surface area, specimen homogeneity, liquid-to-solid ratios, and curing periods in compacted cement-stabilized soil. The experimental approach plan in Figure 16 is followed to investigate Cr(VI) leaching in cement-stabilized soil and the factors influencing this process.

3.2 Materials and Methods

3.2.1 Materials

Volcanic cohesive soil was sourced from Chiba Prefecture, Kanto region, Japan (Figure 15a). Its basic properties were determined following Japanese Geotechnical Society standards. A commercially available cement-based stabilizer, primarily composed of ordinary Portland cement with pozzolanic and hydration additives like blast furnace slag and gypsum, was used (Figure 15b).



(a)



(b)

Figure 15 a) Volcanic soil b) ordinary Portland cement

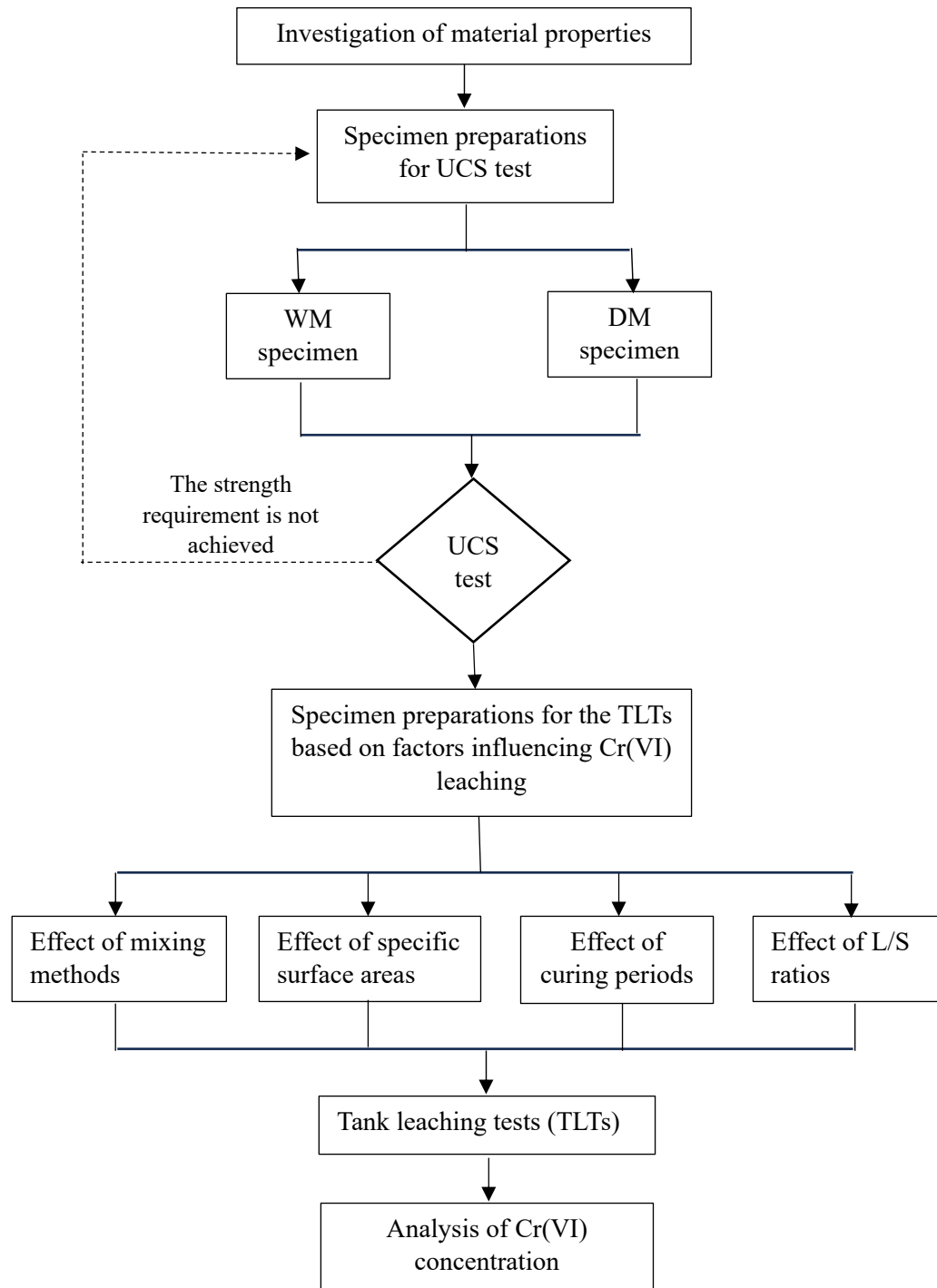


Figure 16 Experimental approach for the preliminary investigation of Cr(VI) from compacted cement-stabilized soil and the factors influencing its leaching

3.2.2 Specimen Preparations for Unconfined Compressive Strength Test (UCS)

Soil stabilization typically uses 50–200 kg/m³ of stabilizer to succeed the strength requirement of 200 kPa/m², according to the Japan International Cooperation Agency (1998). In this study, cement contents were selected based on the mixing method

- Dry mixing method (DM): The specimen was prepared by mixing clay with stabilizer content of 100 kg/m³ in initial water.
- Wet mixing method (WM): the specimen was prepared by mixing clay with stabilizer content of 200 kg/m³ at a water-to-cement ratio (W/C) of 0.7.

The water, cement, and soil were mixed by Hobart mixer to achieve uniform distribution. WM producing more homogeneous mixtures than DM. Specimens were cured under fully sealed conditions for 7 and 28 days to evaluate strength development over time.

3.2.3 Specimen Preparations for Tank Leaching Tests (TLTs)

This study examined factors influencing Cr(VI) leaching from compacted cement-stabilized soil using tank leaching tests (TLTs). Cement contents were selected based on unconfined compressive strength (UCS) test results to meet strength requirements. Four key factors were considered:

- Mixing Methods: The specimens for DM and WM were prepared same as UCS test.
- Specific Surface Areas: Two specimen types were prepared shaped (S) and split (SP) specimens, to assess the effect of surface area on Cr(VI) concentration (Figures 17a, 17b). Specimens were prepared according to JCAS L-01:2006. The S specimens (50 mm diameter, 100 mm height) were compacted in three layers with 12 blows. The SP specimens were split into four sections (50 mm diameter, 25 mm height each), increasing the specific surface area by 1.6 times. Each section was compacted using 9 blows.
-

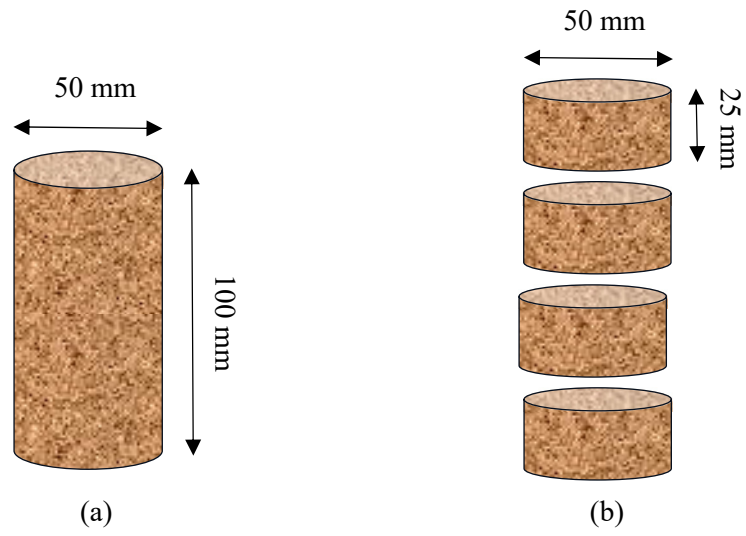


Figure 17 a) S specimen and b) SP specimen

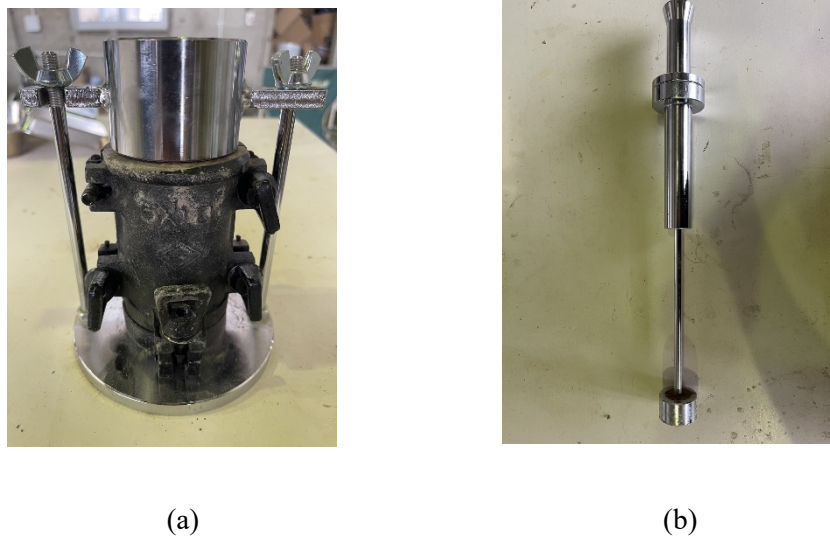


Figure 18 a) standard mold (50 mm in diameter and 100 mm in height) and b) rammer

- Effect of Curing Periods

This research investigated the effects of curing periods on the leaching of Cr(VI) from the compacted cement-stabilized soil. Specimens were cured for 7 and 28 days under fully sealed conditions (see Figure 19) to study the impact of hydration reactions during both the early and late stages.



Figure 19 The specimen cured for 7 and 28 days

- Effect of Liquid-to-Solid Ratios (L/S)

The L/S ratio is a crucial factor in leaching tests that affects the efficiency. High L/S ratios can lead to more extensive leaching and better simulation of worst-case scenarios but may result in diluted leachate. Low L/S ratios might underestimate leaching potential but provide higher contaminant concentrations in the leachate. In this research, leaching tests were conducted with different L/S ratios of 5 and 10 ml/g, respectively, to investigate the influence of L/S ratio on the leaching of Cr(VI). This approach helps to understand how varying amounts of water affect the release of Cr(VI) from the specimen, providing insights into its potential environmental impact. Table 4 shows the specimen preparation under various conditions, taking into account influential factors affecting the leaching of Cr(VI).

Table 4 Sample preparation program.

Sample preparation program	Cement-stabilized soil							
	S specimen (50×100, Dia. × H (mm))				SP specimen (50×25, Dia. × H (mm) ×4 specimens)			
Mixing method	WM ($W/C=0.7$)		DM		WM ($W/C=0.7$)		DM	
Content of the stabilizer (kg/m ³)	200		100		200		100	
Curing period (Days)	28 and 7		28 and 7		28 and 7		28 and 7	
Liquid-to-Solid ratio (ml/g)	10, 5	10, 5	10, 5	10, 5	10, 5	10, 5	10, 5	10, 5

3.2.4 Unconfined Compressive Strength Test (UCS)

The UCS test followed the JGS standard using both WM and DM specimens, cured in fully sealed conditions for 7 and 28 days. Tests were conducted after the designated curing periods, aiming for achieving strength requirement for 200 kPa/m² at 28 days.

3.2.5 Tank Leaching Test

This study investigated Cr(VI) leaching concentration from stabilized soil with cement using S and SP specimens for different conditions. Specimens were soaked in distilled water (pH~7) at two different L/S ratios (See Table 4) within a polymer tank. In this study, liquid-to-surface area (L/A) was not conducted but the L/S ratio was used in TLT to account for potential surface area changes due to erosion during soaking.

Rather than the standard 28-day immersion per the Ministry of Construction (2000) guidelines, a partial leachate replacement method was applied (Figure 20). Leachate replacement, kept under 10% of the total volume, was conducted at cumulative times of 0.25, 1, 3, 7, 10, 14, 24, and 28 days.

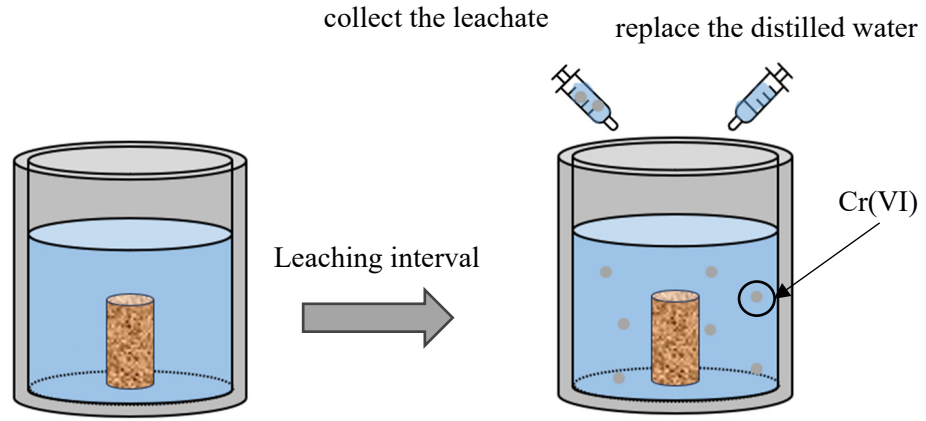


Figure 20 The modified procedure of the tank leaching test for immersing specimen for 28 days

Equations (26)–(27) to analyze the Cr(VI) leaching behavior. Collected leachate was filtered through a 0.45 μm membrane filter and analyzed using the diphenylcarbazide absorption method to determine Cr(VI) concentration.

$$\delta = C_{Pre}V_{Pre} + [C_{Be}V_T - C_{Pre}(V_T - V_{<10\%})] \quad (26)$$

$$C_i = \frac{\sum \delta}{V_T} \quad (27)$$

Where δ represents the total change in concentration during leaching interval; C_{Pre} is the concentration of the leachate from the previous leaching interval; V_{Pre} is volume of leachate from the previous leaching interval; C_{Be} is concentration of leachate before the current leaching interval measurement; V_T is total volume of leachate; $V_{<10\%}$ is partial replacement of leachate under 10% of total volume of leachate, and C_i is cumulative concentration at the end of the current leaching interval.

3.2.6 Analysis of Cr(VI) Concentration

The concentration of Cr(VI) was analyzed using the absorptiometric method with diphenyl carbazide, following the JIS (Japan Industrial Standards) K 0102. An absorption

wavelength of 540 nm was employed using the shimadzu UVmini-1240 UV/Visible Scanning Spectrophotometer.

3.3 Results and Discussions

3.3.1 Material Properties

The soil's basic properties were determined according to Japanese Geotechnical Society standards. It had a water content of 92%, a wet unit weight of 1.32 g/cm³, and a particle density of 2.69 g/cm³. The liquid and plastic limits were 121% and 90%, respectively. A commercially available cement-based stabilizer, such as cement composed with blast furnace slag.

3.3.2 UCS Test Results

Figure 21 presents the UCS results for WM and DM specimens cured for 7 and 28 days. Both methods showed similar strengths with same curing periods. After 28 days of curing, UCS values for both methods remained consistent.

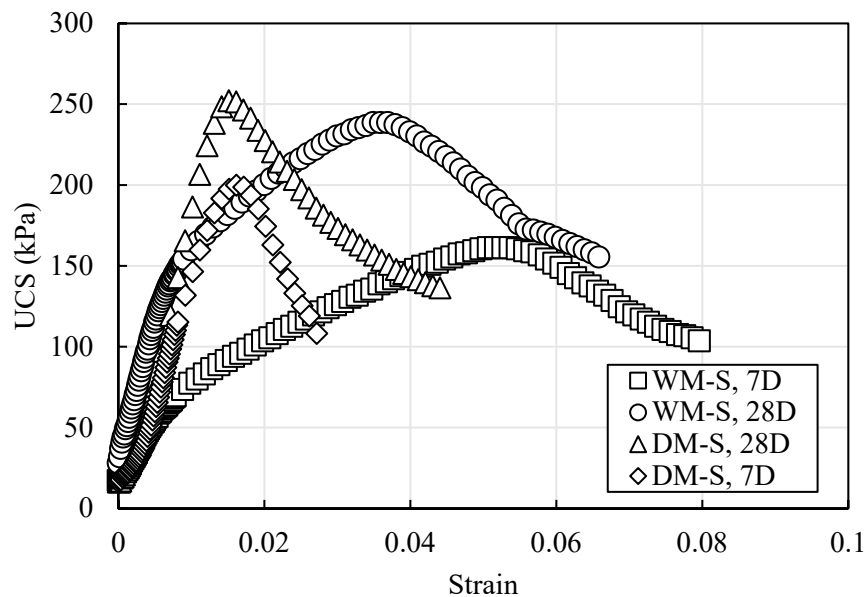


Figure 21 Strength of cement-stabilized soil with different methods and curing periods

3.3.3 pH and EC of Leachate

Figure 22 shows that the pH values of WM and DM specimens consistently increased, indicating the leaching of alkaline-soluble hydration products, such as Ca²⁺. WM exhibited

higher pH values than DM, with 7-day cured specimens showing higher pH than those cured for 28 days. This is due to the higher stabilizer content in WM, which produces more cementation products like $\text{Ca}(\text{OH})_2$. In the initial 24 hours, a significant amount of $\text{Ca}(\text{OH})_2$ quickly dissolved into the leachate. After 7 days, the pH stabilized, suggesting that $\text{Ca}(\text{OH})_2$ dissolution had reached saturation. This trend aligns with the findings of (Sun et al., 2022)

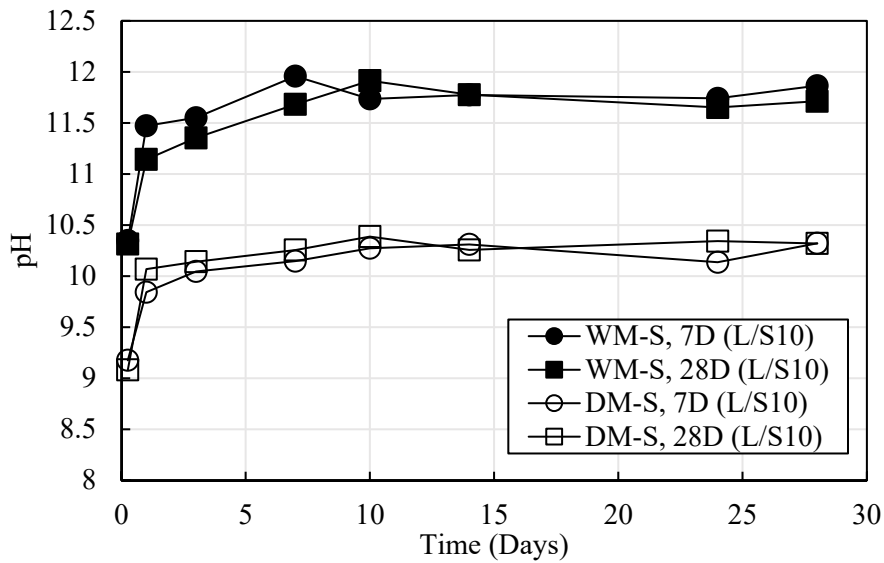


Figure 22 Leachate of pH against with time for WM and DM with different curing periods

Figure 23 illustrates the electrical conductivity (EC) trends in leachate from WM and DM specimens, both of which showed a consistent increase. WM had higher EC values than DM, with 7-day cured specimens displaying higher EC than those cured for 28 days. This is because the 7-day specimens were still in the early stages of hydration, leading to ongoing hydration product formation and limited stabilization, resulting in higher EC in the leachate. In contrast, 28-day cured specimens exhibited lower EC values due to the immobilization of soluble constituents in the later stages of hydration.

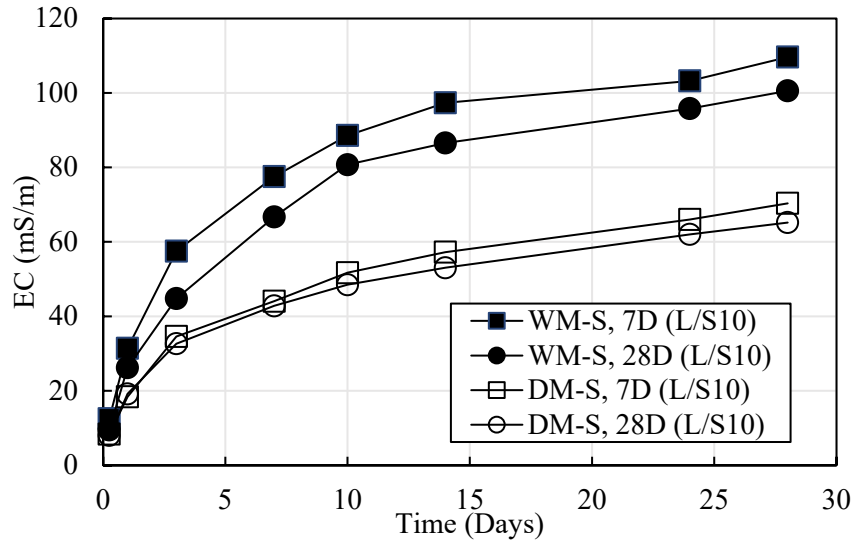


Figure 23 Leachate of EC against leaching time for WM and DM with different curing periods

In this study, different cement contents were used depend on the mixing methods. For WM, Cr(VI) leaching was below detectable concentration. This suggests that the higher cement content (200 kg/m^3) enhances hydration reactions, such as the production of Ca(OH)_2 , leading to increased in pH of leachate. The pH of the WM have over exceeded 11 (See Figure 22). Cr(VI) can be precipitated as calcium chromate (CaCrO_4) through a reaction with Ca(OH)_2 . (Wang & Vipulanandan, 2000). For DM, the lower cement content (100 kg/m^3) resulted in less Ca(OH)_2 generation due to a weaker hydration reaction. This is reflected in the lower pH values of DM compared to WM, which suggests that a certain amount of Cr(VI) may leach out into the leachate.

3.3.4 Effect of Curing Period

Figure 24 shows that curing periods significantly influence the reduction of Cr(VI) leaching concentrations. Specimens cured for 28 days exhibited a lower concentration of Cr(VI) leaching compared to those cured for 7 days. The longer curing period facilitated the formation of hydration products, which effectively immobilized Cr(VI) within the specimen. This suggests that a curing period longer than one week is crucial for cement-stabilized soil to minimize potential environmental risks.

During the TLTs, conducted by immersing specimens for 28 days, the highest Cr(VI) leaching concentrations occurred before the 28th day, typically around 10–14 days. This is because Cr(VI) diffuses from the pore spaces and near-surface regions of the stabilized soil into the solution. Around 10–14 days, weakly bound or surface-near Cr(VI) reaches equilibrium in the solution, causing a peak concentration. After this peak, Cr(VI) near the surface or in accessible pore spaces is leached out, and the remaining Cr(VI) diffuses more slowly. Additionally, some Cr(VI) may adsorb back onto the specimen surface or form insoluble compounds, reducing its concentration in the leachate over time. These concentrations exceeded Japan's environmental regulation limit of 0.02 mg/L for Cr(VI), suggesting that the current TLT method, which only measures leaching concentrations after 28 days, may underestimate actual Cr(VI) leaching during critical earlier periods.

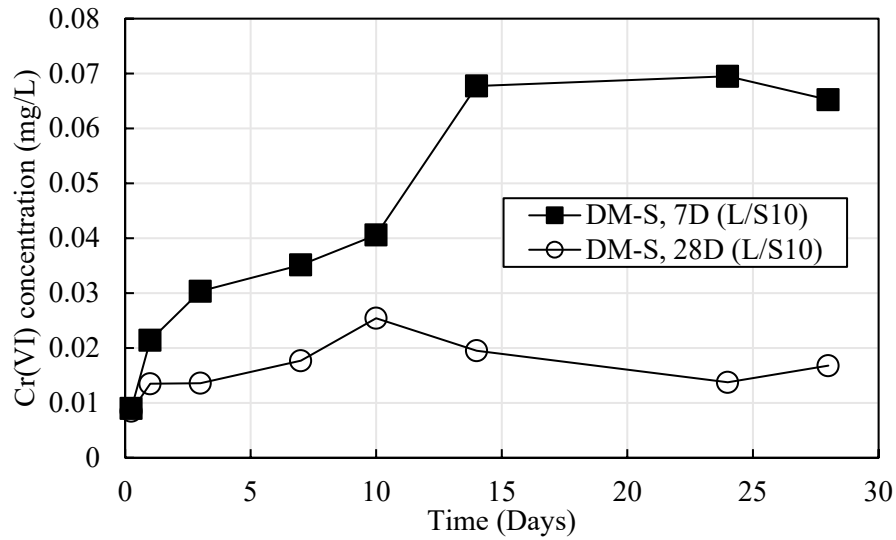


Figure 24 Cr(VI) concentration against leaching time for cement-stabilized soil with different curing periods

3.3.5 Effect of L/S ratios

Figure 25 illustrates the effect of L/S ratios on Cr(VI) leaching from compacted cement-stabilized soil. The results show that the L/S ratio significantly influences Cr(VI) leaching. A higher L/S ratio of 10 ml/g leads to greater Cr(VI) leaching compared to a lower L/S ratio of 5 ml/g. This is due to increased solvent availability, enhanced diffusion, larger concentration gradients, and more favorable equilibrium dynamics. This insight is essential for designing leaching tests and evaluating the environmental impact of Cr(VI) in different scenarios.

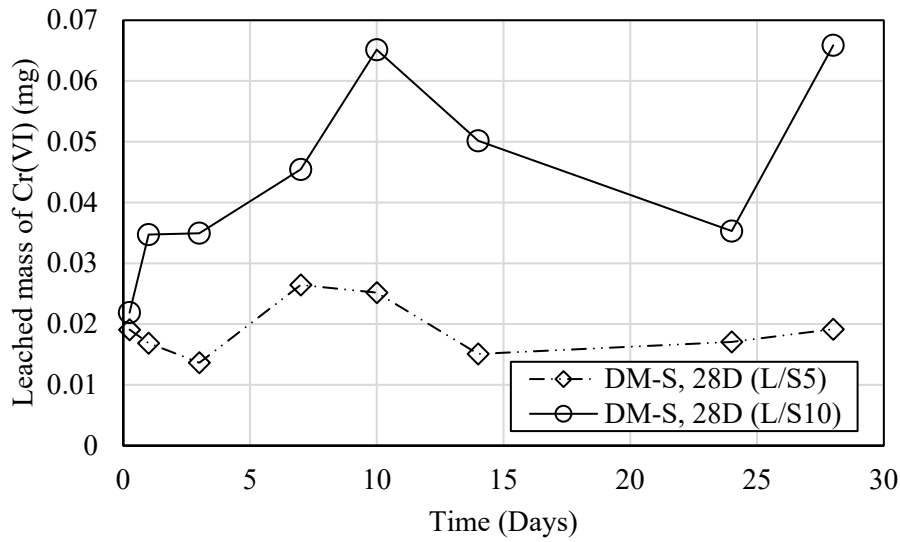


Figure 25 Cr(VI) concentration against leaching time for cement-stabilized soil with different L/S ratios

3.3.6 Effect of Specific Surface Area

Figure 26 shows that the SP specimens resulted in the higher Cr(VI) leaching concentration, while the S specimens exhibited the lower concentration. All specimens followed a similar trend, separated into four periods: First period: The concentration of Cr(VI) increased rapidly with time. Second period: The concentration of Cr(VI) decreased with time. Third period: Cr(VI) concentrations stabilized at a steady level. Fourth period: The concentration of Cr(VI) increased gradually with time.

For third and fourth periods, Cr(VI) begins to adsorb onto the specimen surface. Additionally, for the split (SP) specimens, the highest concentration occurred at 7 days of leaching, faster than for shaped (S) specimens, where the highest concentration occurred at 10 days. These results indicate that increasing specific surface area leads to a faster leaching rate.

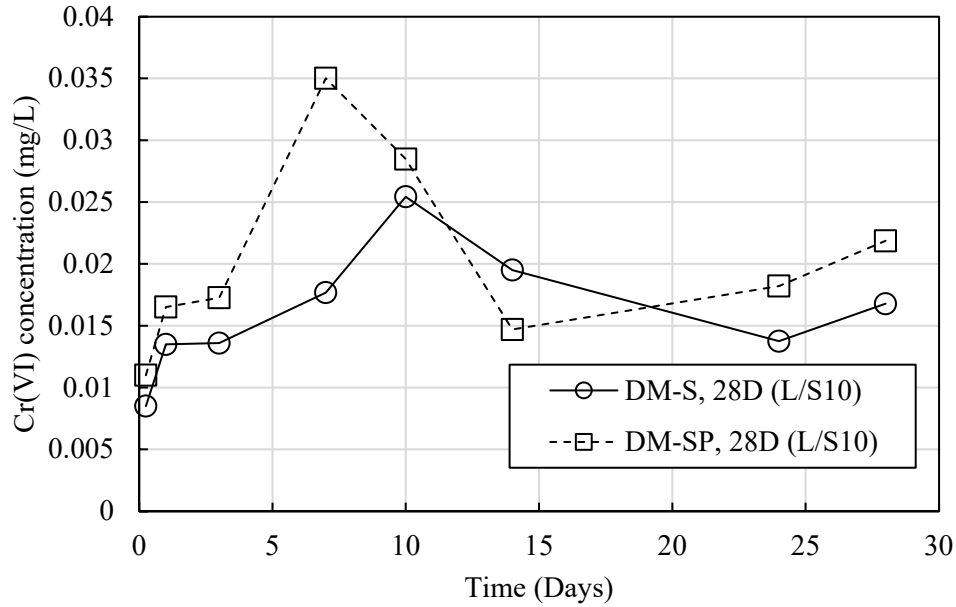


Figure 26 Cr(VI) concentration against leaching time for cement-stabilized soil with different specific surface areas

3.4 Conclusions

This study investigated Cr(VI) leaching in cement-stabilized soil, considering factors like mixing methods, curing periods, surface areas, and liquid-to-solid ratios. Cr(VI) leaching was significantly lower in WM specimens compared to DM specimens with similar unconfined compression strength. In WM, Cr(VI) was undetectable due to enhanced cement hydration and specimen homogeneity. The current TLT, which measures leaching concentrations after 28 days of immersion as per Japanese regulations, may underestimate Cr(VI) leaching, as peak concentrations occur before 28 days. Additionally, specimens cured for 7 days exhibited higher Cr(VI) leaching than those cured for 28 days, due to increased precipitation from hydration products like $\text{Ca}(\text{OH})_2$. This highlights the need for a curing period of at least one week in cement-stabilized soil to mitigate environmental risks. A higher specific surface area leads to faster leaching rates. Considering these factors is crucial for setting appropriate TLT regulations.

Chapter 4: Investigating the Mechanical and Leaching Performance of Stabilized Clay Compacted with RCA

4.1 Introduction

In this chapter, recycled concrete aggregate (RCA) will be added to compacted cement-stabilized clay (SC) in varying amounts (20%, 40%, and 60% by weight) to enhance mechanical performance and reduce leaching performance. The experimental approach plan in Figure 27 is followed to investigate the mechanical properties and Cr(VI) leaching resulting from the addition of RCA to cement-stabilized clay.

4.2 Materials and Methods

4.2.1 Materials

The RCA obtained by crushing concrete structures (ordinary Portland cement, W/C = 50%) and particle size control to suit its particle size distribution to that of C-40 in JIS A 5001. The clay used in this study was generated at an excavation site in Osaka, Japan, and may contain small amounts of cement and bentonite. The geotechnical properties of RCA and clay were determined according to Japanese Geotechnical Society standards.

4.2.2 Specimen Preparation and Mix Design

The RCA was adopted to enhance the mechanical properties of stabilized clay (SC), including to promote waste recycling, and reduce the cost associated with cement usage. Consequently, in this study, Portland blast furnace slag cement Type B (BB cement), as regulated by JIS R 5211, was used as a stabilizer at a content of only 50 kg/m³. SC was prepared by mixing the clay (with its initial water content) and BB cement using a Hobart mixer until homogeneous, curing it for 7 days in a sealed condition, and then roughly crushing it with a hammer. The SC

was mixed with different RCA contents for 20%, 40%, 60% and 80% by dry weight, as well as SC and RCA separately.

4.2.3 Compaction Test

The compaction performance and mixture compatibility of the composite soil are closely tied to fundamental mechanical properties, namely stiffness and strength development (Lipiec et al., 2009; Cabalar & Mustafa, 2017). According to JIS A1210 standards, for RCA content with a maximum particle size of 37.5 mm, the standard Proctor compaction tests of Type B were conducted on the SC with RCA contents of 0%, 20%, 40%, and 60% (dry-mass basis), respectively. The mixtures were prepared using the dry mixing method. Firstly, the RCAs were thoroughly mixed with dry SC. Then, water was added to the mixtures, followed by compaction with 55 blows/layer distributed over three layers within a standard mold of 150 mm in diameter and 125 mm in height. This compaction process utilized a 4.5 kg rammer with a drop height of 300 mm, corresponding to an energy input of 550 kJ/m³.

4.2.4 Hydraulic Conductivity Test

The effects of the RCA contents on hydraulic conductivity of the compacted SC-RCA mixtures were evaluated. Hydraulic conductivity is one of the significant properties of construction materials, in addition to compaction performance to encompass hydraulic conductivity characteristics as well (Głuchowski et al., 2018). Considering the achievements in previous research, the hydraulic conductivity of the composite soil tends to sharply increase when the contents of coarse aggregate are as high as 50% (Shaker & Elkady, 2015; Al-Moadhen et al., 2018). Therefore, current research has adopted the hydraulic conductivity tests of the compacted SC with different RCA contents of 0%, 20%, 40% and 60%, respectively, to investigate the effect of RCA contents, which result in different gradation and porosity of the SC-RCA mixtures, as well as the links between hydraulic conductivity and leaching characteristics. The specimens were saturated with distilled water in a vacuum chamber, and

then subjected to the falling head hydraulic conductivity tests, according to JGS 0031, until the hydraulic conductivity of the SC-RCA mixture was constant.

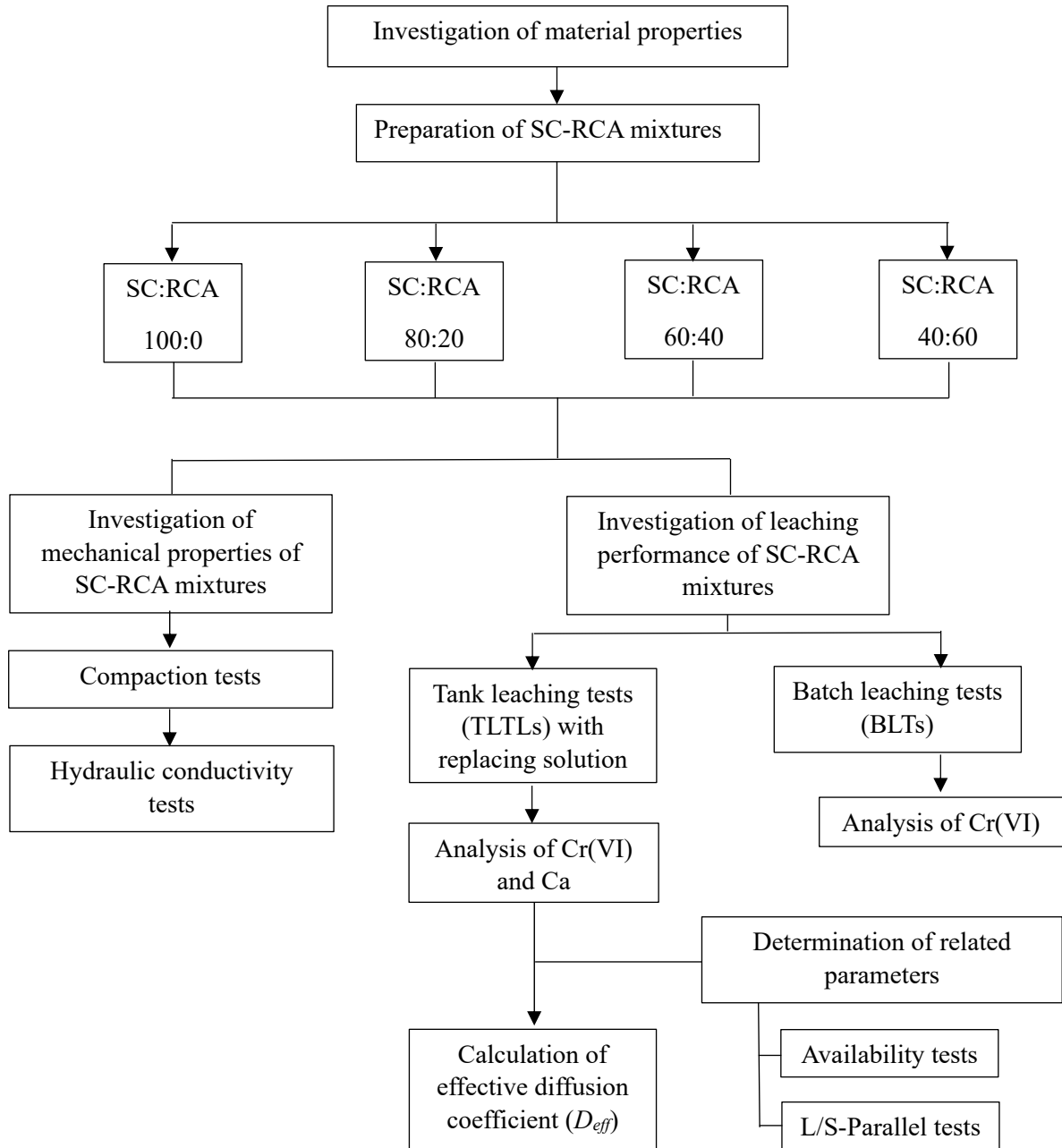


Figure 27 Experimental approaches for investigating the mechanical and leaching performance of stabilized clay compacted with RCA

4.2.5 Conventional Batch Leaching Test

The conventional batch leaching tests (BLT) was conducted with different SC-RCA mixtures which is 20%, 40%, 60%, 80% RCA , as well as SC and RCA separately. This procedure aimed to establish a standardized criterion ensuring comparability of leaching behavior with increase RCA contents. In accordance with the regulations stipulated in Public Notice No. 46, JEA. The liquid to solid ratio of 10 ml/g was employed, and the specimen was crushed to particles below 2 mm in size. Distilled water was used as the liquid medium, with an initial pH value maintained at a neutral level (pH~7). The specimen was soaked with distilled water in 1-liter plastic bottles and subjected to a 6-hour mixing period by horizontally shaking the bottles at a speed of 200 rpm. Subsequently, the solid phase was separated from the liquid phase using a centrifuge machine at a gravitational acceleration of 3000 for 20 minutes. Following the centrifugation process, the clear liquid phase was filtered using a 0.45 μm membrane filter.

4.2.6 Tank Leaching Test

The tank leaching test (TLT) primarily aims to capture leaching behaviors of monolithic and/or compacted low-permeable specimens. Generally, it involves the periodic replacement of the entire leach solution. This intermittent replacement aids in estimating the leaching mechanism of the COCs by measuring changes in concentration over fractions of time. In this test, the compacted SC-RCA mixtures at the same proportions as those employed in the hydraulic conductivity tests, as well as uncompacted granular RCA were included to assess the immobilization of Cr(VI), and other soluble cation (Ca), through compaction of the SC-RCA mixtures. The cylindrical PVC molds, 150 mm in diameter and 70 mm in height, were prepared and filled with the SC-RCA mixtures at their optimum moisture content. A polymer mesh with a 0.45 μm opening covered the exposed surface area to prevent specimen erosion during the leaching test, as shown in Figure 28a. For the uncompacted granular RCAs, 500 g of the granular RCAs was wrapped within a polymer mesh sheet (0.45 μm opening), as illustrated in Figure

28b. The leaching tests were carried out at a liquid-to-surface area ratio (L/A) of 10 ml/cm² for compacted SC-RCA mixtures, and at L/S of 10 ml/g for granular RCAs. During the testing period, the leachates were completely replaced at cumulative periods of 0.25, 1, 4, 9, 16, and 36 days. The procedure of replacement is shown in Figure 29. This experimental approach follows previously established tank leaching test methods (Hill et al., 2001; Kamon et al., 2003; Inui et al., 2008).

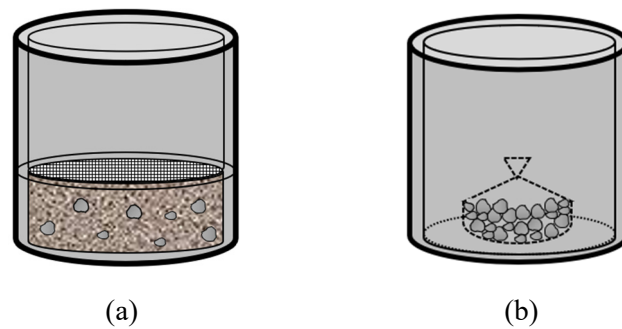


Figure 28 Schematic of the TLT; a) compacted SC-RCA mixtures, and b) Uncompacted-Granular RCAs

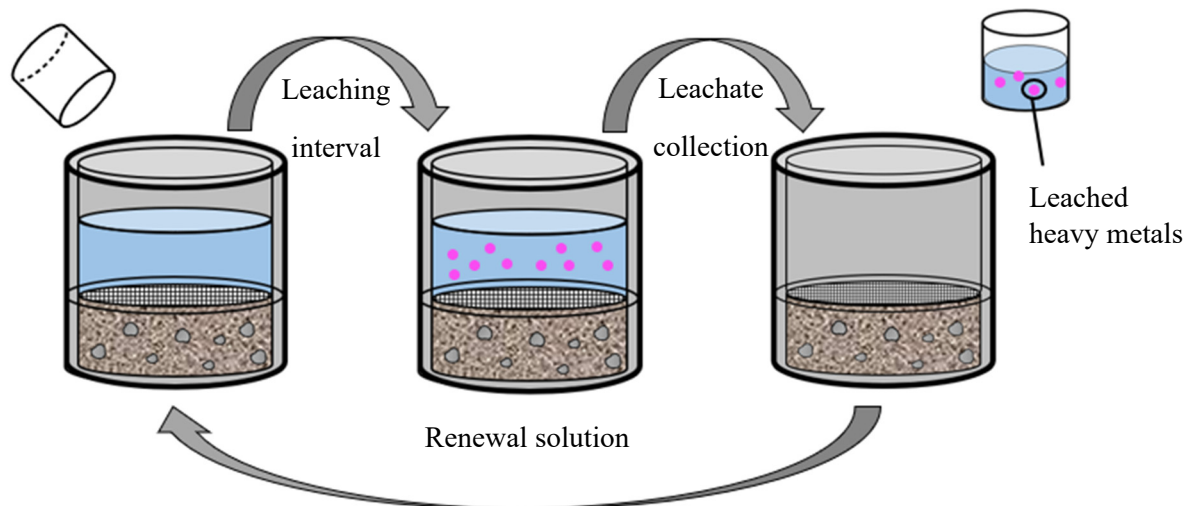


Figure 29 The procedure of the TLT

4.2.7 Availability Test

The availability can be expressed as the mass fraction of potentially leachable contaminants per unit dry mass of the sample. In this study, the available tests were conducted for the different SC-RCA mixtures, including 0%, 20%, 40% and 60% RCA, following a method for the alkaline waste/secondary materials, proposed by the Japan Society of Material Cycles and Waste Management. The sample was crushed until the particle size became under 0.125 mm. This method comprises two extraction steps. First, the sample and distilled water were stirred at a high L/S of 50 ml/g. The pH of the leachate was monitored after approximately 10 minutes stirring. If the leachate pH falls below 6.5, sodium hydroxide solution is added to maintain the pH between 6.5 and 7.5. If the pH is 6.5 or higher, the pH is not adjusted, and stirring continues for 3 hours. After 3 hours, filtration of the leachate is conducted using a 0.45 μm membrane filter. Second, the remaining sample after the first extraction is mixed with distilled water at a L/S of 50 again, and the leachate pH is monitored after 10 minutes stirring. If the pH of the leachate falls below 11.9, sodium hydroxide solution is added to maintain the pH between 11.9 and 12.1. If the leachate pH is above 11.9, the pH is not adjusted. After 3 hours, the leachate is filtered and combined for analysis. The sum of the contaminants extracted in these two steps accounts for the potentially leachable mass in the alkaline material.

4.2.8 L/S-Parallel Test

The L/S-parallel test was conducted through a series of conventional batch leaching test with different L/S ratios of 2, 5, 10, 20, and 50 ml/g. The different SC-RCA mixtures, including 0%, 20%, 40%, and 60% RCA, were crushed to particles below 2 mm in size. Soil samples were placed into 1-liter plastic bottles with distilled water to meet the required L/S ratio. These bottles were then placed on a horizontal shaker and shaken at 200 rpm for 24 hours (Tang et al., 2020; Sakanakura et al., 2021). Following the shaking process, the bottles were left standing for 15 mins. Subsequently, the leachate was filtered using 0.45 μm membrane filter.

4.2.9 Determination of Cr(VI) and Ca Concentrations

The concentration of Cr(VI) was analyzed using the absorptiometric method with diphenyl carbazide, following the JIS (Japan Industrial Standards) K 0102. An absorption wavelength of 540 nm was employed using the Shimadzu UVmini-1240 UV/Visible Scanning Spectrophotometer. Concentrations of Na and Ca were analyzed using Microwave Plasma Atomic Emission Spectroscopy (MP-AES) with a model 4210 instrument manufactured by Agilent Technologies, Inc., USA.

4.3 Results and Discussions

4.3.1 Material properties

The RCA obtained by crushing concrete structures (ordinary Portland cement, W/C = 50%) and particle size control to suit its particle size distribution to that of C-40 in JIS A 5001. Figure 30 presents the particle size distribution of the SC-RCA mixtures, which has a maximum particle size of 37.5 mm. The clay used in this study was generated at an excavation site in Osaka, Japan, and may contain small amounts of cement and bentonite. The geotechnical properties of RCA and clay were determined according to Japanese Geotechnical Society standards and are summarized in Tables 5 and 6. Table 7 shows mixing design of SC-RCA mixtures with different RCA contents.

Table 5 Properties of RCA

Property	Value
Particle density (Mg/m^3)	2.56
Maximum dry density, $\rho_{d_{max}}$ (Mg/m^3)	1.54
Minimum dry density, $\rho_{d_{min}}$ (Mg/m^3)	1.44
Maximum porosity, n_{max} (-)	0.44
Minimum porosity, n_{min} (-)	0.40
Water absorption (%)	10.76
Initial water content (%)	2.21

Table 6 Properties of Clay

Property	Value
Particle density (Mg/m^3)	2.70
Liquid limit (%)	46.4
Plastic limit (%)	37.5
Initial water content (%)	39.6

Table 7 Mixing design of SC-RCA mixtures with different RCA contents

Mixtures	SC (%)	RCA (%)
SC : RCA	100	0
	80	20
	60	40
	40	60
	20	80
	0	100

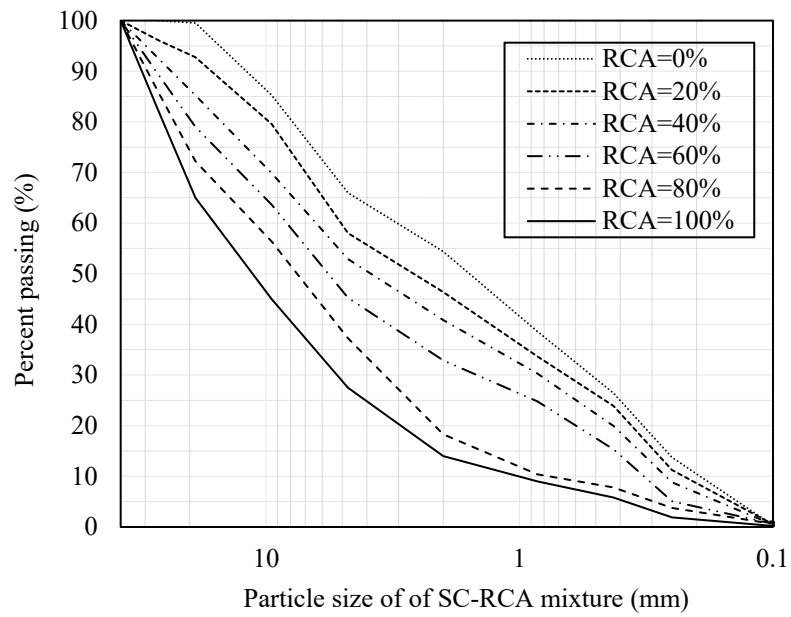


Figure 30 Grain size distributions of SC-RCA mixtures

4.3.2 Effect of RCA Content on Compaction Performance of SC

The specific volumes of compacted SC-RCA mixtures with different RCA contents are shown in Figure 31. It was found that RCA content significantly contributed to the improvement in compaction performance. As the proportion of RCA in the mixture increased, the specific volume decreased, while moisture content also decreased. This indicates that the addition of RCA content in compacted SC-RCA mixtures has a significant influence on reducing the total void ratio within the specimen.

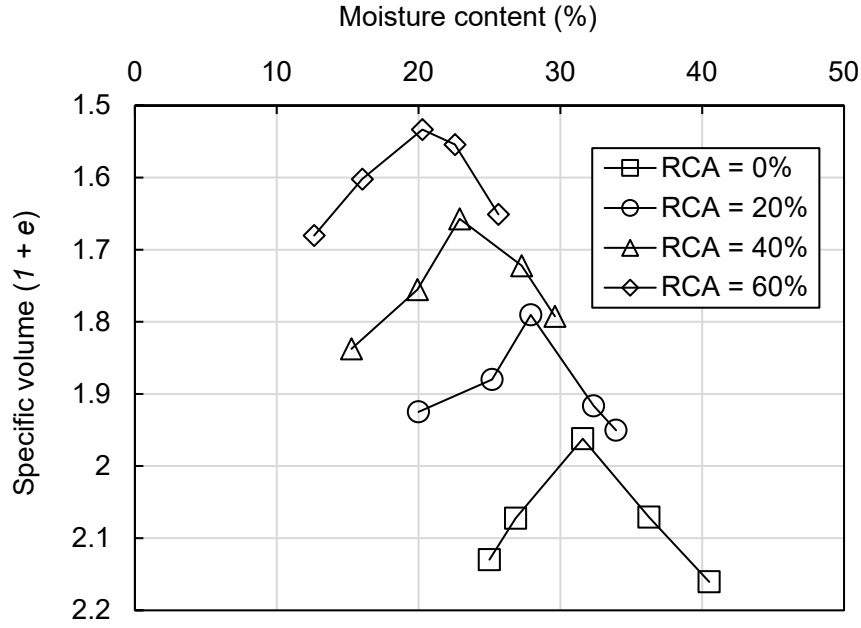


Figure 31 Specific volume of compacted SC-RCA mixtures with various RCA contents

4.3.3 Effect of RCA Content on Hydraulic Performance of SC

Figure 32 presents the hydraulic conductivity coefficients (K) of compacted SC with 20%, 40%, and 60% RCA, as well as solely SC. It is evident that increasing RCA content enhanced the compaction performance of SC, resulting in a significant decrease in hydraulic conductivity. The results showed that the K continued to decrease until reaching a minimum at 40% RCA content. However, at 60% RCA, the K increased. This phenomena can be explained by porosity variation of SC and RCA, the porosity of SC and RCA contents in compacted specimen in this study can be calculated by correlation of volume of voids divided by the volume of solid as shown the following Equation (26) to (27).

$$n_{SC} = \frac{V_v}{V_{SC} + V_v} \quad (28)$$

$$n_{RCA} = \frac{V_v}{V_{RCA} + V_v} \quad (29)$$

where n_{SC} is the porosity of SC; n_{RCA} is the porosity of RCA; V_{SC} is volume of SC in specimen (m^3); V_{RCA} is volume of RCA in specimen (m^3) and V_v is volume of voids in specimen (m^3). The variation in those results in compacted SC with RCA can be explained by dividing them into four stages: At 0% RCA content, the K is controlled by the n_{SC} of compacted SC. At 20% RCA content, in the compacted state of SC-RCA mixtures, the SC between RCA particles consolidated under higher confining stress, becoming stiffer compared to other parts of the SC (Tavakoli et al., 2010; Lu et al., 2021). This is consistent with n_{SC} remaining almost unchanged, indicating local compaction of the SC matrix. As shown in Figure 33, the interconnected SC bridges between RCA particles within the specimen formed denser network structures. These denser SC bridges decreased the K within the specimen. At 40% RCA content, with further addition of RCA, the distance between RCA particles decreased, leading to a slight increase in n_{SC} because the SC matrix became partially isolated by RCA particles. Additionally, as RCA is an impermeable material, this reduction in the distance between RCA particles increased the flow path at the interface between SC and RCA inside the specimen, resulting in a decrease in K to some extent. At 60% RCA content, the n_{RCA} was almost equal to n_{maxRCA} (see Table 5). A granular skeleton forms as RCA particles contact each other, causing the SC matrix to become trapped in voids between the RCA assemblies, which prevented the SC matrix from being compacted. This resulted in increased n_{SC} , leading to an increase in K . These findings are consistent with previous studies (Tavakoli et al., 2010; Al-Moadhen et al., 2018; Lu et al., 2021).

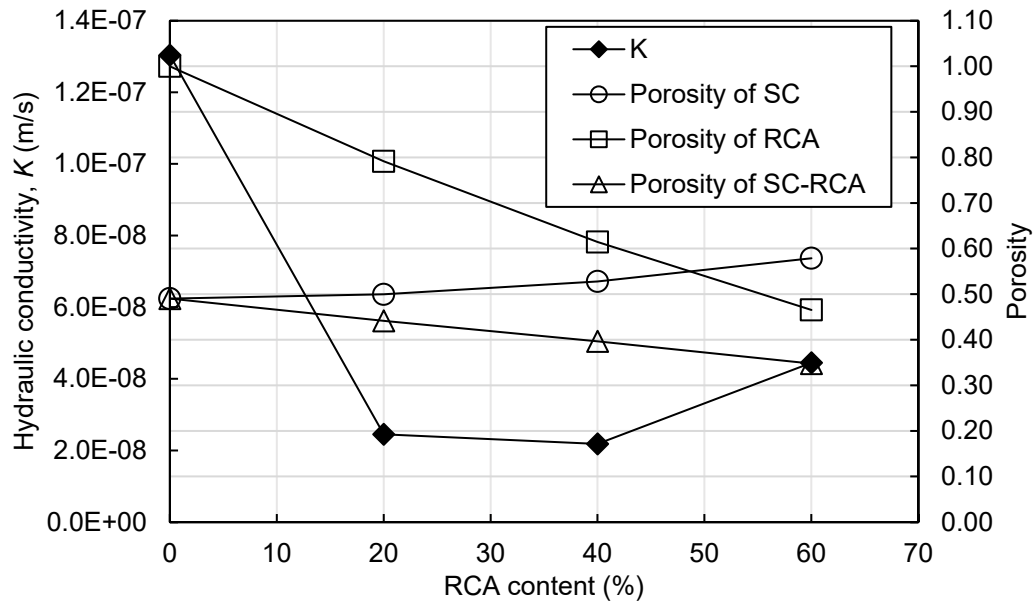


Figure 32 The hydraulic conductivity and porosity variations of compacted SC with various RCA contents

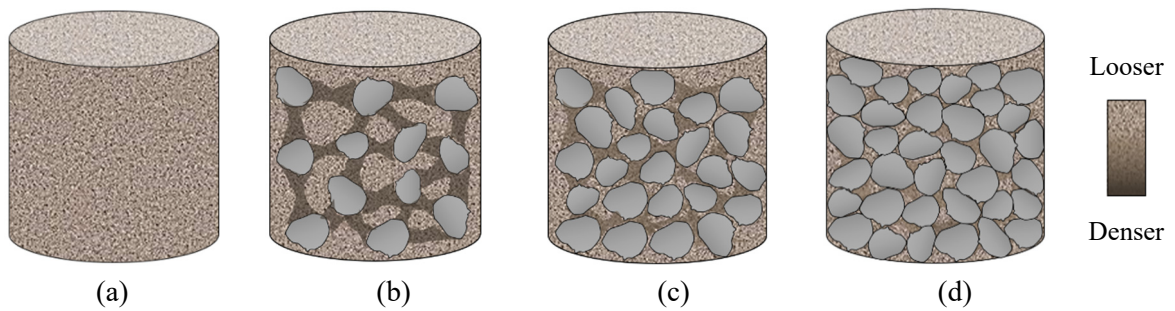


Figure 33 The meso-structure of compacted SC with various RCA contents; a) RCA = 0%, b) RCA = 20%, c) RCA = 40%, and d) RCA = 60%

4.3.4 Conventional Batch Leaching Test Results

Table 8 illustrates the leaching concentration of Cr(VI) in the BLT, conducted for crushed RCA and SC with particle sizes under 2 mm. The highest leaching concentration of Cr(VI) was observed in the pure RCA specimen, followed by the RCA-SC mixtures with 60%, 40%, and 20% RCA, respectively. Interestingly, the specimens with pure RCA and RCA-SC mixtures with 60% and 40% RCA exceeded the Japanese environmental regulation limit of 0.02

mg/L for Cr(VI) leaching concentration. These results indicate that the source of Cr(VI) leached out from RCA, as Cr(VI) was undetectable in the pure SC specimen. However, previous research suggests that conventional batch leaching tests with particle sizes under 2 mm may have overestimated the leaching concentration of Cr(VI) under field conditions, as grain size can influence the leaching behavior (Inui et al., 2008; Chai et al., 2009). Thereby, in this study, to evaluate leaching characteristics of Cr(VI) under field conditions, a compacted specimen was utilized, comprising both uncompacted-granular RCA, to assess the immobilization characteristics of Cr(VI). This evaluation focused on comparing the compatibility and compaction of the RCA-SC mixture with granular RCA without compaction.

Table 8 Cr(VI) concentration with various RCA contents in the BLT

Element	RCA content in SC-RCA mixture (%)				
	0	20	40	60	100
Cr(VI) (mg/L)	ND	0.018	0.023	0.028	0.037

4.3.5 Tank Leaching Test Results

Table 9 shows the mass of Cr(VI) and Ca leached from different specimen forms in the TLTs. To observe results across different specimen forms, leaching concentrations were converted into mass leached by calculating based on RCA mass for Cr(VI), since RCA is the source of Cr(VI) according to BTLT results (see Table 8), and based on SC-RCA mass within the specimen for Ca. Leaching amounts of both Cr(VI) and Ca were observed, due to its large specific surface area, which led to the rapid dissolution of Cr(VI) and Ca from RCA particles into the leachate. However, the compacted SC-RCA mixtures did not show detectable amounts of Cr(VI) but clearly exhibited leaching amounts of Ca. These results indicate that the leached amounts of both Cr(VI) and Ca from the granular RCAs could be reduced by adding them to the compacted SC-RCA mixtures. This suggests that the addition of RCA can effectively improve

the compaction performance of the SC-RCA mixture, as well as potentially limit the leaching amounts of both Cr(VI) and Ca.

Table 9 Cumulative eaching amounts of Cr(VI), Ca with different cumulative leaching times

List	Time (Days)	RCA content in compacted SC (%)				Granular RCAs
		0	20	40	60	
	0.25	ND	ND	ND	ND	0.21
Cumulative leaching	1	ND	ND	ND	ND	0.33
amounts of Cr(VI)	4	ND	ND	ND	0.01	0.40
(mg/kg)	9	ND	ND	ND	0.01	0.47
(RCA dry-mass basis)	16	ND	ND	ND	ND	0.54
	36	ND	ND	ND	ND	0.62
	0.25	290	98	77	225	5,050
Cumulative leaching	1	835	290	301	527	11,270
amounts of Ca	4	1,349	879	750	1,151	26,790
(mg/kg)	9	1,573	1,349	1,107	1,655	45,770
(SC-RCA dry-mass basis)	16	1,718	1,753	1,401	2,107	67,300
	36	2,065	2,222	1,798	2,617	91,000

ND is the undetectable

Table 10 illustrates the relationship between pH and EC (Electrical Conductivity) over cumulative leaching time. The leachate from all specimens exhibited similar trends in pH and EC changes, indicating continuous leaching of alkaline substances and concentration leaching in the solid phase. There was a gradual increase in both pH and EC of the leachate, stabilizing at 36 days for all specimens. The pH and EC decreased when the granular RCAs were mixed in the compacted SC-RCA mixtures, which aligns well with the leaching amounts of both Cr(VI) and Ca.

Table 10 Leaching of pH and EC with different cumulative leaching times

List	Time (Days)	RCA content in compacted SC (%)				Granular RCAs
		0	20	40	60	
pH	0.25	7.65	7.53	7.33	8.02	10.88
	1	9.87	8.04	7.67	8.61	11.13
	4	10.61	10.79	9.09	10.95	11.20
	9	10.98	10.75	10.46	11.35	11.26
	16	11.12	10.91	10.89	11.18	11.20
	36	11.13	11.29	11.28	11.27	11.29
EC (mS/cm)	0.25	3.71	1.18	1.18	1.93	15.01
	1	3.83	1.98	1.47	3.06	20.77
	4	8.16	8.74	8.50	12.12	23.77
	9	14.81	13.04	11.10	12.56	25.93
	16	18.60	14.87	14.86	14.73	28.60
	36	30.53	33.31	31.97	33.10	48.30

4.3.6 Dominant Leaching Mechanism

As the amounts of Cr(VI) in the leachate was nondetectable in many cases, determining the leaching mechanism for Cr(VI) proved impossible. Consequently, further analysis will focus on the leaching amounts of Ca. Additionally, to assess the leaching mechanism of compaction SC-RCA mixtures, thereby the leaching amounts from granular RCAs are disregarded, as shown in Table 11. The slopes of correlation between the cumulative mass released of Ca and cumulative leaching time under a logarithm function for compacted SC with 0%, 20%, 40% and 60% RCA are shown in Table 11. These slopes ranged from 0.35 to 0.65, indicating that the dominant leaching mechanism for these specimens was diffusion (de Groot & van der Sloot, 1992). The D^{app} of Ca was further analyzed according to Equation (25). The results revealed

that the D^{app} of Ca decreased with increasing RCA content until reaching a maximum at 40%. However, at 60% RCA content, the D^{app} of Ca exhibited an increase. This phenomenon can potentially be explained by D_{eff} (discussed later).

Table 11 The D^{app} of Ca from compacted SC with various RCA contents

Element	RCA content (%)	Slope	Leaching mechanism	ρ_{d_m} (kg/m ³)	C_{av} (mg/kg)	D^{app} (m ² /s)
Ca	0	0.37	Diffusion	1,371	2,741	4.90E-13
	20	0.62	Diffusion	1,487	4,894	6.01E-14
	40	0.63	Diffusion	1,590	7,047	2.44E-14
	60	0.50	Diffusion	1,701	9,200	3.20E-14

4.3.7 Effective Diffusion Coefficient

The ad/desorption parameters such as M_T and K_d of Ca and Cr(VI), are shown in Table 12 which were obtained by fitting with linear regression between C_r and M_L , obtained from the L/S parallel test with various L/S ratios. The results revealed that M_T and K_d increased as RCA content increased. The R_d of compacted SC with 20%, 40%, 60% of RCA and without RCA was determined using Equation (13). The results revealed that the R_d was higher as RCA content increased, as shown in Table 13. The D_{eff} values, calculated using Equation (12), were 1-2 orders of magnitude larger than the D^{app} values, demonstrating that some Ca may be adsorbed onto solid phase and longer leaching time to the leachate.

In Table 14, the D_{eff} of Ca from compacted SC-RCA mixtures decreased until reaching a minimum at 40% RCA content, due to the poor pore connectivity of SC-RCA mixtures blocking diffusion. However, at 60% RCA, the D_{eff} of Ca increased. This phenomenon can be explained by considering the meso-structural distribution and hydraulic performance. The

enhanced pore connectivity of well-connected RCA particles led to an increase in K , facilitating quicker and more direct pathways for Ca to diffuse through the SC-RCA matrix. These results suggest that a 40% RCA content significantly improves the compaction performance of SC and effectively limited the leaching concentration of chemicals of concern.

Table 12 Ad/Desorption parameters of Ca and Cr(VI) from compacted SC with various RCA contents

RCA content (%)	K_d (L/kg)		M_T (mg/kg)	
	Ca	Cr(VI)	Ca	Cr(VI)
0	4.07	-	2044	-
20	7.73	21.78	3169	0.467
40	11.58	19.09	4480	0.642
60	15.62	17.98	5992	0.989

Table 13 The R_d of Ca from compacted SC with various RCA contents

Element	RCA content (%)	Particle density (Mg/m ³)	n_{SC-RCA}	ρ_{dm} (g/cm ³)	R_d (Ca)	R_d (Cr(VI))
Ca	0	2.69	0.49	1.37	12.39	-
	20	2.66	0.44	1.49	27.07	74.44
	40	2.63	0.40	1.59	47.56	77.76
	60	2.61	0.35	1.70	77.28	88.83

Table 14 The calculated D_{eff} of Ca from compacted SC-RCA with different RCA contents

Element	RCA content (%)	C_{av}	D_{eff} (m ² /s)
Ca	0	2,741	6.01E-12
	20	4,894	1.63E-12
	40	7,047	1.16E-12
	60	9,200	2.45E-12

4.4 Conclusion

This research explores the reuse of recycled concrete aggregate (RCA) as a geotechnical material to improve the compaction performance of stabilized clay (SC) while mitigating Cr(VI) leaching from RCA. The findings demonstrate that RCA inclusion significantly influences both the mechanical properties and leaching behavior of SC-RCA mixtures. The addition of RCA enhanced the compaction performance of SC-RCA mixtures, leading to a reduction in hydraulic conductivity (K). The lowest K value was achieved with 40% RCA content, which represents the optimal mixture composition. At 60% RCA, the minimum void ratio was observed, but the increased contact between RCA particles trapped the SC matrix in voids, preventing proper compaction. This increased porosity within the SC matrix led to higher hydraulic conductivity, emphasizing the importance of balancing RCA content to achieve desired hydraulic properties.

Leaching tests revealed notable differences in Cr(VI) and Ca behavior between granular RCAs and compacted SC-RCA mixtures. Granular RCAs exhibited leaching of both Cr(VI) and Ca, primarily due to their large specific surface area facilitating rapid dissolution. In contrast, compacted SC-RCA mixtures showed no detectable Cr(VI) leaching and reduced Ca leaching, underscoring their effectiveness in mitigating contaminant release. These results highlight RCA's dual role in enhancing compaction performance and minimizing leaching.

The D_{eff} for Ca in compacted SC-RCA mixtures were 1-2 orders of magnitude larger than apparent diffusion coefficients (D_{app}), indicating significant Ca adsorption onto the solid phase and extended leaching times. At 40% RCA content, D_{eff} reached its minimum due to poor pore connectivity, which effectively blocked diffusion. However, at 60% RCA, meso-structural changes and enhanced pore connectivity increased both D_{eff} and K , allowing faster and more direct pathways for Ca diffusion through the SC-RCA matrix.

In conclusion, RCA incorporation into SC-RCA mixtures improves compaction performance while mitigating leaching of Cr(VI) and Ca. The findings emphasize the need to carefully optimize RCA content to balance hydraulic and diffusion properties, demonstrating the potential of SC-RCA mixtures as sustainable and effective geotechnical materials.

Chapter 5: Modeling and Practical Analysis

5.1 Introduction

The parameters obtained from the previous chapter, combined with select values from the literature review, were utilized in the analytical modeling to predict the long-term leaching behavior of calcium (Ca) and Cr(VI) and explore practical applications. Figure 34 below outlines the modeling approach employed in this analysis.

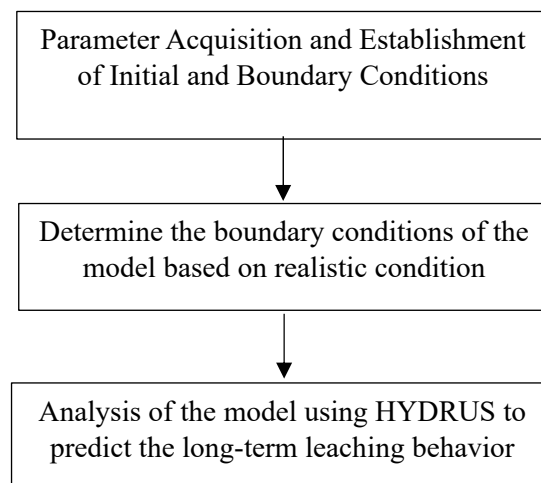


Figure 34 Analytical modeling approaches for contaminant transport from Stabilized clay-RCA

5.2 Analytical Modeling

5.2.1 Parameter Acquisition and Establish the Initial and Boundary Conditions

Table 15 shows the parameters used in the modeling are evaluated based on laboratory results and supplemented by values obtained from a comprehensive literature review. This dual approach ensures that the model is grounded in both experimental data and established research, providing a robust basis for predicting leaching performance and understanding key factors affecting the behavior of SC-RCA mixtures. The boundary conditions of the model are

configured to simulate constant water infiltration from the top, percolate through the model, and interact with the horizontal groundwater flow.

Table 15 Parameters from laboratory results and literature reviews used for analytical modeling

Input parameter	Source
Dry density, ρ_{d_m}	Compaction test (Chapter 4)
Hydraulic conductivity, K	Hydraulic conductivity test (Chapter 4)
Porosity, n	Compaction test (Chapter 4)
Volumetric water content, θ_v	Compaction test (Chapter 4)
Effective diffusivity for Ca, D_{eff}	Tank leaching test (Chapter 4)
Molecular diffusivity, D_0	Equation (10)
Tortuosity, τ (-)	Equation (27)
Longitudinal dispersivity, α_L	Equation (28)
Transverse dispersivity, α_T	Equation (29)
Portioning coefficient, K_d	L/S-Parallel test (Chapter 4)
Initial concentration C_0	L/S-Parallel test (Chapter 4)
Saturated water content, θ_s	Zhang et al. (2017); Mahdi (2018)
Residual water content, θ_r	Zhang et al. (2017); Mahdi (2018)
Inverse of the air entry suction, α	Zhang et al. (2017); Mahdi (2018)
Empirical shape parameter, n_E	Zhang et al. (2017); Mahdi (2018)
Negative pressure head, ψ	Equation (31)

In the HYDRUS software, molecular diffusivity (D_0) is utilized as a key parameter to model solute diffusion in the absence of other transport mechanisms. D_0 represents the intrinsic diffusivity of a solute, reflecting its movement due to concentration gradients within a medium, independent of advection, dispersion, or other external forces. This molecular diffusivity serves

as the foundational parameter for solute transport in the model, providing a starting point for simulations. In this research, D_0 can be calculated by D_{eff} divided by τ , according to Equation (10) which D_{eff} values obtained from chapter 4.3.7. and τ values can be determined from following equation (28)

$$\tau = \frac{\Theta v^{7/3}}{n^2} \quad (27)$$

where Θ_v is volumetric water content and n is porosity.

Groundwater contamination is a major environmental concern, particularly in cases where pollutants migrate through soil and aquifers. One of the key factors influencing contaminant movement is hydrodynamic dispersion, which describes how a chemical spreads due to both mechanical mixing and molecular diffusion. To quantify dispersion, longitudinal dispersivity (α_L) and transverse dispersivity (α_T) are used to predict how far and wide a chemical plume will spread over time (Sharma & Reddy, 2004).

The α_L represents contaminant spreading along the groundwater flow direction, driven by velocity variations. A common assumption in contaminant transport modeling is that the α_L is approximately 10% of the total chemical plume length as shown in Equation (29).

$$\alpha_L = 0.1 \times L_{plume} \quad (28)$$

where α_L is longitudinal dispersivity (cm) and L_{plume} is the total length of the chemical plume (cm). However, the α_T describes lateral spreading, mainly influenced by molecular diffusion. It is typically 10% of longitudinal dispersivity as showed in Equation 30.

$$\alpha_T = \frac{\alpha_L}{10} \quad (29)$$

where α_T is transverse dispersivity (cm).

Initial conditions of model are comprised of pressure head and initial concentration. For Initial concentration parameter can be calculated by using parameter from L/S-Parallel test in Chapter 4 as shown in following equation (31)

$$C_0 = \frac{M_T \times M_S}{M_S K_d + V_w} \quad (30)$$

where C_0 is initial concentration (mg/cm^3); M_S is mass of solid (kg) and V_w is volume of water (cm^3). The positive pressure head at a certain depth below the water surface (or water table) is determined by the height of the water column above that point. The negative pressure head (ψ), is determined by Van Genuchten equation, which describes the relationship between the Θ_v and ψ as shown in Equation (32);

$$\Theta_v = \Theta_r + \frac{\Theta_s - \Theta_r}{[1 + (\alpha|\psi|)^{n_E}]^{1-1/n}} \quad (31)$$

The C_0 is set in the stabilized layer, as it originates from the stabilized clay-RCA mixtures.

5.2.2 Analysis of Model Using Hydrus

In this research, the movement of contaminants is predicted using advection-dispersion finite element (FE) analysis. HYDRUS is a computer program that solves the one-dimensional advection-dispersion equation (See Equation (17)) for layered systems of finite or infinite extent (Radcliffe & Simunek, 2010). Through this solution, HYDRUS calculates contaminant concentrations over time at specified observation points. The prediction of contaminant movement is modeled over 100 years, with the observation point chosen at the location of the highest concentration near the groundwater flow, to prevent environmental impacts from the leachate of stabilized soil into the groundwater.

5.3 Results and Discussions

5.3.1 Parameters used for Modeling

The results obtained from the previous section, along with certain parameters from the literature review, were incorporated into the analytical modeling. This section focuses on the long-term prediction of contaminant migration. Table 16 shows the boundary position at A of the model was set as a constant flux to simulate water infiltration, while boundaries at D and F were assigned different constant pressure heads to simulate horizontal groundwater flow, as shown in Figure 35. Table 17 presents the soil hydraulic parameters used in this model for the stabilized clay, and the neighboring sandy soil (see Figure 35).

Table 16 Position and condition of boundary on model

Boundary position	Boundary condition	value
A	Constant flux (cm/year)	50
B	No flux (-)	-
C	No flux (-)	-
D	Constant pressure head (cm)	140
E	Constant pressure head (cm)	122
F	No flux (-)	-

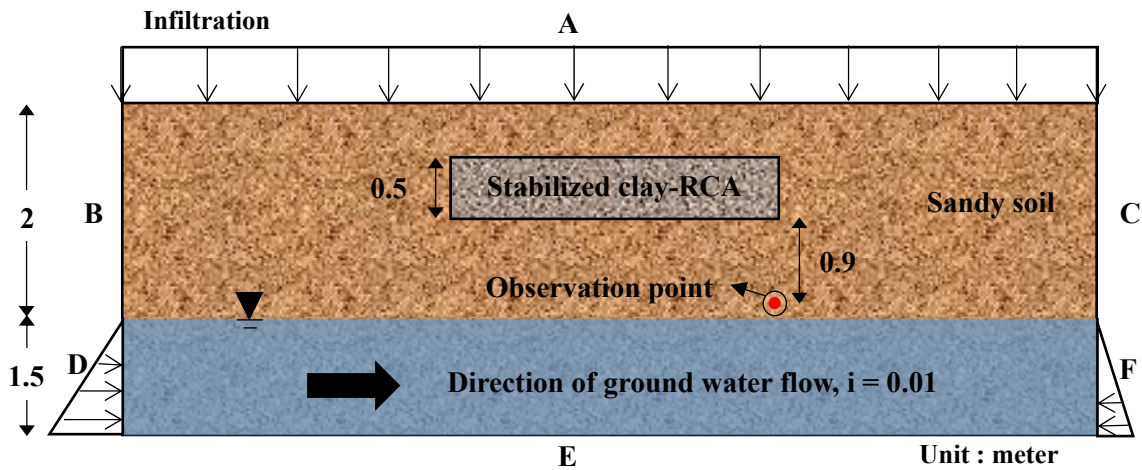


Figure 35 Cross section assumed in the analytical study

Table 17 Hydraulic parameters for stabilized SC-RCA mixtures and sandy soil

List of parameter	RCA content in compacted SC (%)				Sandy soil
	0	20	40	60	
Dry density, (Mg/m^3)	1.37	1.49	1.59	1.70	1.61
Hydraulic conductivity, K (cm/year)	411	77.34	68.85	140.37	662,696
Porosity, n (-)	0.49	0.44	0.40	0.35	0.36
Volumetric water content, θ_v (-)	0.43	0.42	0.36	0.35	0.25
Tortuosity, τ (-)	0.58	0.68	0.58	0.70	0.30
Saturated water content, θ_s (-)	0.478	0.478	0.478	0.478	0.377
Residual water content, θ_r (-)	0.108	0.108	0.108	0.108	0.095
Inverse of the air entry suction, α (1/cm)	0.001	0.001	0.001	0.001	0.029
Empirical shape parameter, n_E	1.695	1.695	1.695	1.695	2.430
Negative pressure head, ψ (cm)	4,603.41	5,457.43	7,268.40	7,753.15	292.21

Table 18 shows the solute transport parameters of Ca and Cr(VI). The influence of RCA on the partitioning behavior of Ca and Cr(VI) in SC-RCA mixtures have been systematically evaluated. The results indicate a contrasting behavior between these two elements, driven by their chemical properties and interactions with the SC-RCA mixtures.

RCA and SC, being rich in calcium-based phases such as calcium hydroxide (Ca(OH)_2), calcium silicate hydrates (C-S-H), and carbonates (CaCO_3), significantly enhance the adsorption of Ca^{2+} . The higher K_d for Ca can be attributed to the strong affinity of calcium ions for the available adsorption sites within the RCA and cementitious matrix. Furthermore, the alkaline conditions introduced by RCA and SC promote the precipitation of Ca^{2+} as calcium carbonate, further contributing to its retention within the solid phase.

In contrast, Cr(VI) exhibits an opposite trend. RCA serves as a primary source of Cr(VI) according to experimental finding from previous chapter. As RCA content increases, more Cr(VI) is released into the leachate, leading to higher aqueous concentrations and, consequently, a lower K_d .

D_0 for Ca was calculated from Equation (10) with parameters from the TLT results, while Cr(VI), originating from the RCA, was undetectable according to the TLT results from the previous section. To ensure environmental safety, the D_0 for Cr(VI) was assumed to be the same as that of Ca, simulating a conservative scenario. The D_0 of 40% RCA specimen is the lowest, as RCA improves compaction, reduces the hydraulic performance of SC, and limits the diffusion of solutes into the leachate.

Table 18 Solute transport parameters of Ca and Cr(VI)

Element	List of parameter	RCA content in compacted SC (%)			
		0	20	40	60
Ca	Effective Diffusivity, D_{eff} (cm/year)	1.895	0.514	0.365	0.772
	Molecular diffusivity, D_0 (cm ² /year)	3.260	0.753	0.633	1.095
	Portioning coefficient, K_d (cm ³ /g)	4.07	7.73	11.58	15.62
	Initial concentration C_r (mg/cm ³)	0.466	0.395	0.379	0.378
	Longitudinal dispersivity, α_L (cm)	9	9	9	9
	Transverse dispersivity, α_T (cm)	0.9	0.9	0.9	0.9
Cr(VI)	Effective Diffusivity, D_{eff} (cm/year)	1.895	0.514	0.365	0.772
	Molecular diffusivity, D_0 (cm ² /year)	3.260	0.753	0.633	1.095
	Portioning coefficient, K_d (cm ³ /g)	ND	21.78	19.09	17.98
	Initial concentration C_r (mg/cm ³)	ND	2.1E-05	3.4E-05	5.5E-05
	Longitudinal dispersivity, α_L (cm)	9	9	9	9
	Transverse dispersivity, α_T (cm)	0.9	0.9	0.9	0.9

5.3.2 Model Analysis Results

Figure 36 and 37 illustrates the concentration of Ca and Cr(VI) leaching from compacted SC-RCA mixtures, measured as the concentration at an observation point (90 cm downgradient from the SC-RCA) over a period of up to 100 years. The compacted SC solely exhibited the highest Ca concentration, followed by compacted SC with 60% RCA, 20% RCA, and 40% RCA. Compacted SC with 40% RCA showed the lowest Ca concentration due to its low D_{eff} , as demonstrated in experimental results. A similar trend was observed for Cr(VI) leaching, though the Cr(VI) leaching from compacted SC solely remained below the concentration limit. As the K_d values of the compacted SC-RCA mixtures increased with RCA contents of 0%, 20%, 40%,

and 60%, the leaching time extended. This is because higher K_d values reflect greater adsorption onto the solid phase, delaying the release of contaminants into the leachate. For Cr(VI), the leaching times for compacted SC-RCA mixtures were similar because its K_d values did not vary significant.

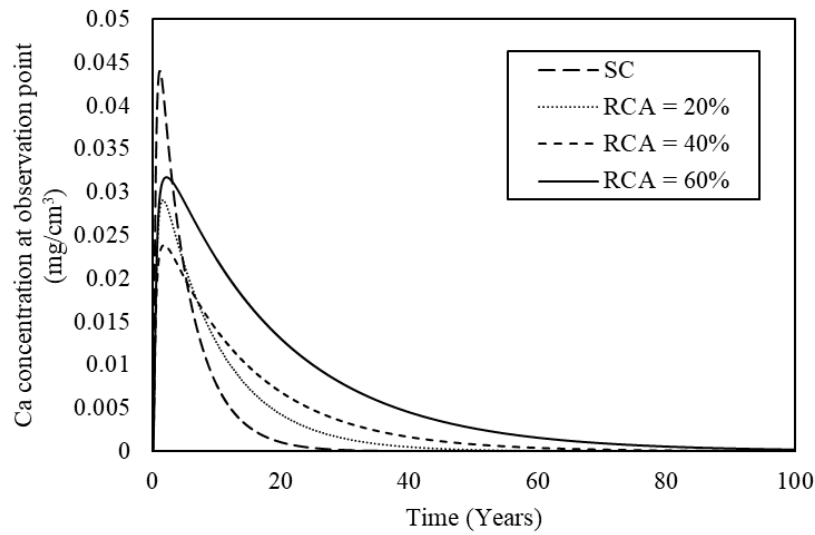


Figure 36 Ca concentration at observation point from the SC-RCA mixtures model

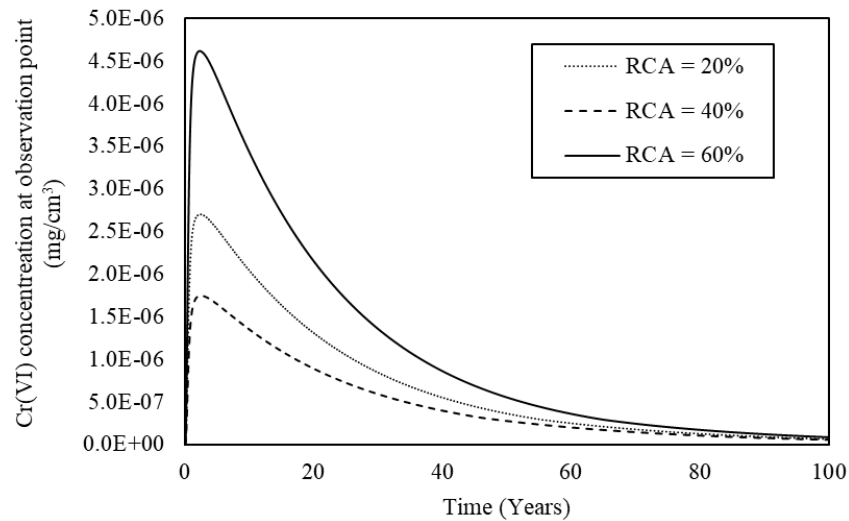


Figure 37 Cr(VI) concentration at observation point from the SC-RCA mixtures model

5.3.3 Practical Applications

Considering that Ca and Cr(VI) transport in SC-RCA mixtures is influenced primarily by diffusion and sorption, the modeled examples clearly show that an increase in D_{eff} leads to higher concentration. The highest D_{eff} in SC resulted in the highest concentration for Ca, which had a lower K_d . However, despite the higher D_{eff} , this did not result in a longer leaching time compared to the RCA 40% model, where the D_{eff} for Ca was the lowest, but the higher K_d led to an extended leaching period. A similar K_d for Cr(VI) resulted in only minor differences in K . Therefore, when significant sorption is expected, it may be more efficient to prioritize the estimation and control of K_d . The modeling results support the findings from TLTs and L/S Parallel tests, which suggest that for the predesign stage, estimating D_{eff} (e.g., from the results presented in this thesis) and determining K_d from L/S-parallel tests may be sufficient.

5.4 Conclusion

This chapter represents the concentration of Ca and Cr(VI) from compacted SC-RCA mixtures at an observation point (90 cm downgradient from the SC-RCA) over a period of up to 100 years by modelling. The modelling results exhibited that Ca and Cr(VI) concentrations for the compacted SC with 40%RCA has lowest concentration since it's lowest effective diffusion coefficient (D_{eff}). However, the Increasing RCA content in compacted SC-RCA mixtures extended the leaching time for Ca due to higher adsorption (K_d values), while Cr(VI) leaching remained consistent across mixtures as K_d values showed minimal variation. Lastly, possible applications for using compacted SC-RCA mixtures as a geo-materials are suggested When substantial sorption is expected, prioritizing the estimation and control of D_{eff} and K_d may be more effective.

Chapter 6: Conclusions and Recommendations

6.1 Conclusions

This research investigates Cr(VI) leaching from compacted cement-stabilized clay and evaluates the mechanical and leaching performances of adding RCA into compacted cement-stabilized clay. Additionally, analysis of solute migration modeling and practical applications. The conclusions are divided into 3 parts as follows;

6.1.1 Leaching of Cr(VI) from compacted cement-stabilized clay and the factors influencing this leaching

- Cr(VI) leaching concentrations were significantly lower in wet-mixed (WM) specimens compared to dry-mixed (DM) specimens with equivalent unconfined compression strength.
- In WM specimens, Cr(VI) was undetectable due to improved homogeneity and enhanced cement hydration.
- Specimens cured for 7 days exhibited higher Cr(VI) leaching concentrations than those cured for 28 days.
- Extended curing periods resulted in enhanced precipitation of Cr(VI) due to hydration products such as $\text{Ca}(\text{OH})_2$, suggesting that more than 1 week of curing is necessary to mitigate environmental impacts.
- Higher L/S ratios (10 ml/g) significantly increase Cr(VI) leaching from cement-stabilized soil compared to lower ratios (5 ml/g). This is due to greater solvent availability, enhanced diffusion, and larger concentration gradients. Understanding these effects is crucial for accurate leaching tests and environmental impact assessments.

- Higher specific surface areas led to quicker Cr(VI) leaching rates, emphasizing the need to consider this factor when assessing environmental risks.
- Current TLT regulations, which measure leaching concentrations after 28 days, may underestimate Cr(VI) leaching, as peak concentrations often occur before this period.

To promote waste recycling and reduce costs associated with cement usage to improve clay, RCA was incorporated to enhance the mechanical performance of stabilized clay. However, both RCA and cement contain certain amounts of Cr(VI), making it necessary to investigate leaching performance to minimize environmental impacts. The following results were drawn from the study:

6.1.2 Mechanical and leaching performance of compacted cement-stabilized clay mixed with RCAs

- The minimum void ratio of compacted SC-RCA mixtures was achieved at 60% RCA content.
- Increasing RCA to compacted SC-RCA mixtures significantly improved compaction performance, as indicated by decreased void ratio and water content, and increased dry density.
- The lowest hydraulic conductivity of compacted SC-RCA mixtures was observed at 40% RCA content.
- Increased RCA content led to denser SC bridges between RCA particles, decreasing hydraulic conductivity. At 60% RCA content, the formation of a granular skeleton increased porosity and hydraulic conductivity due to improper compaction of the SC matrix.
- The highest Cr(VI) leaching concentration was found in the pure RCA sample, followed by SC-RCA mixtures with 60%, 40%, and 20% RCA.

- Pure RCA and mixtures with 60% and 40% RCA exceeded the Japanese regulation limit for Cr(VI) leaching (0.02 mg/L). Cr(VI) primarily leaches from RCA, as it was undetectable in pure SC.
- The leaching amounts of Cr(VI) from RCA and Ca from SC-RCA mixtures can be effectively reduced by adding RCA to the compacted SC-RCA mixture. The compacted SC-RCA mixtures showed no detectable Cr(VI) and reduced Ca leaching.
- The D_{eff} values, which were 1-2 orders of magnitude larger than the D^{app} values for compacted SC with 20%, 40%, 60% RCA, as well as without RCA, suggest potential Ca adsorption onto the solid phase and longer leaching times to the leachate.
- D_{eff} of Ca decreased to a minimum at 40% RCA due to poor pore connectivity blocking diffusion. At 60% RCA, D_{eff} increased due to better pore connectivity, leading to higher hydraulic conductivity and more direct pathways for Ca diffusion.

Since solute transport parameters obtained from laboratory results, the long term leaching behaviors for 100 years were investigated via analytical modeling for practical applications. The following results were drawn from the study:

6.1.3 Modelling Analysis and Practical Applications

- The addition of 40% RCA to compacted SC-RCA mixtures enhances mechanical performance, decreases D_{eff} , and reduces the concentrations of Ca and Cr(VI), with results that align closely with experimental findings.
- Increasing RCA content in compacted SC-RCA mixtures extended the leaching time for Ca due to higher adsorption (K_d values), while Cr(VI) leaching remained consistent across mixtures as K_d values showed minimal variation.
- During predesign of compacted SC-RCA, primarily focusing on D_{eff} and K_d may be more effective.

6.2 Recommendations

The results of this research demonstrate the effective use of RCA to improve the mechanical properties and limit the leaching performance of SC.

- RCA has demonstrated its effectiveness in improving the performance of cement-stabilized clay, other recycled materials such as reclaimed asphalt pavement and crushed brick should be considered for further study.
- The mechanical performance, such as compaction, of the compacted SC-RCA mixtures has been evaluated. However, the compressive strength should be comprehensively investigated for practical applications.
- The effects of RCA content on the hydraulic performance of SC have been investigated. Further studies should expansively examine the impact of confining pressure and RCA particle size gradation on the hydraulic performance of SC to comprehensively understand the evolution mechanism and the internal relationship between compactability and hydraulic conductivity.
- TLTs conducted by replacing the entire solution for SC-RCA mixture in this research were performed with distilled water (pH around 7). Future studies could examine the effect of pH by varying the pH of the eluent in tank leaching tests to observe the oxidation reaction of cementitious materials on the leaching of Cr(VI).
- TLTs conducted by replacing the entire solution for the SC-RCA mixture were performed at the optimum water content within the specimens. Future work could investigate the effects of saturated versus unsaturated specimens and their diffusive behavior for both organic and inorganic contaminants.

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